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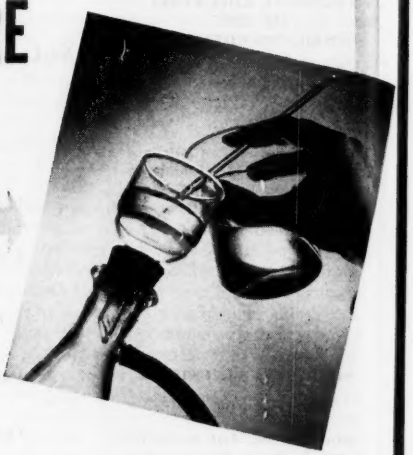

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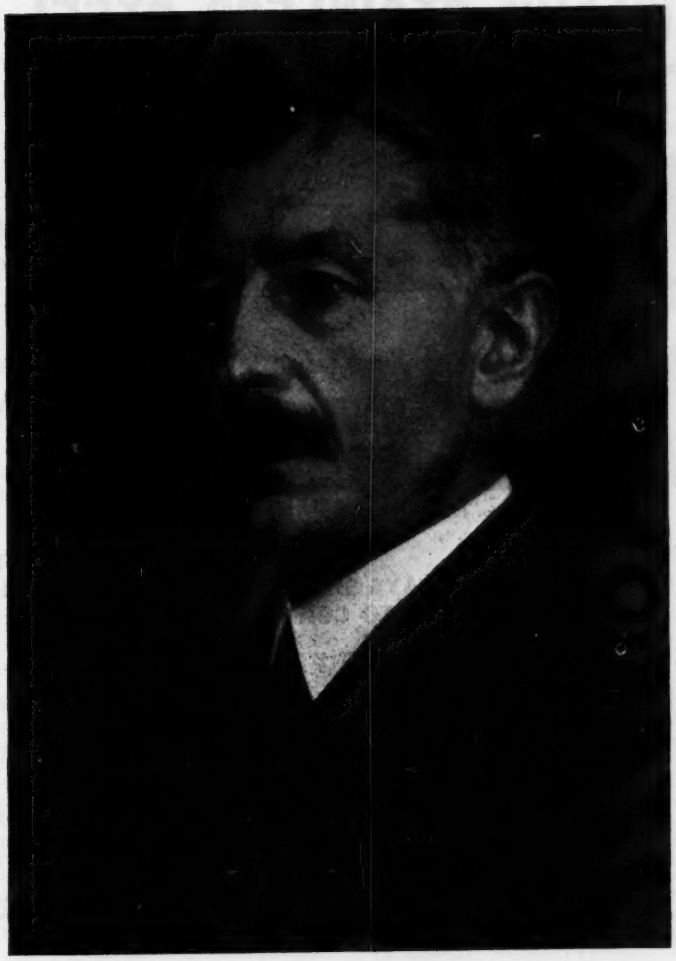

Paul Karrer (1889–)

(*See page 392*)

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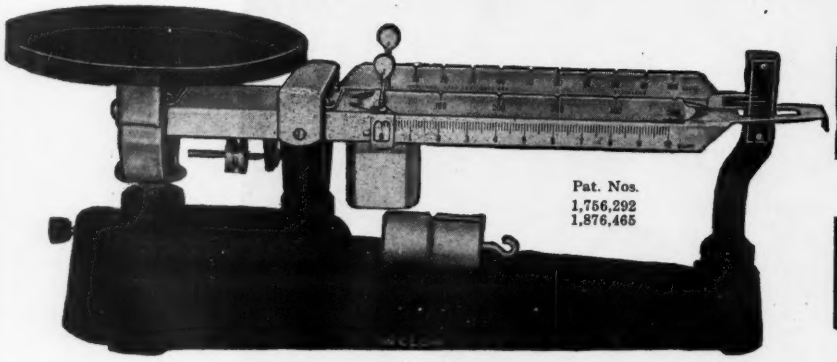

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Editor's Outlook

IF I may paraphrase a more illustrious character, "I'm a disgusted man." Disgusted that my friends and acquaintances are not more articulate.

A few months ago I raised a well-meant objection to the use of the terms "atomic energy" and "atomic bomb." I know when I'm licked. For better or for worse these terms have been adopted into our vocabulary—in fact, one might say into our technical nomenclature. Perhaps the boys at Oak Ridge and Hanford and Chicago should have been perfecting the language along with the methods of production, but they evidently didn't. At any rate, the bomb suddenly burst upon us before anyone had given a good, concentrated thought to naming it, and we took the path of least resistance.

Nevertheless, I'd compromise and settle even for "atom bomb" if it would keep us from going to such ridiculous lengths as we now are.

Pictures from Bikini show an "atomic cloud." Elsewhere, "General McAuliffe says 'nuts' to the atom." Advertisers urge us to buy an "Atomic Diary." Accounts of Army Ordnance experiments hint at "atom-headed rockets." A firm, "Atom, Inc.," has already appeared. The contest of "Man vs. The Atom" is supposed to be in progress. Yesterday's adjective, "super-duper," is today's "atomic," and I am expecting any day to find a comic strip on the adventures of "Tommy the At."

If outbursts from over-excited reporters were all we had to deal with, it would be bad enough. But whatever it is, it seems to be contagious and infects those who ought to know better. One of the most eminent authorities is frightened "when a few cities are atomically destroyed." *Life* says that "officers share the general wish that no human lives will be sacrificed to the atom, now or ever again." And Science Service boasts of its reportorial "coverage of the atom," and surmises that "atoms will be popping elsewhere"—not only at Bikini but in Congress, for example.

Making a mountain out of a mole hill? Perhaps. but for some time we have considered it an objective of science education to bring scientific ideas to the public precisely and accurately, without making them lurid by verbal inflation. And now some of the best of us make public statements which don't say at all what we mean, because it is too much trouble to do a better job.

Of course, those who know what it is all about recognize how much "journalistic license" is being taken, but some people are getting their primary conceptions fixed by these ridiculous phrases, and everyone knows how hard it is to root out a mistaken idea once it is settled. Fairy stories have their place, but many a youngster has a painful time growing out of the Santa Claus complex, and many another continues to look up to the sky and say, "Hello, Mr. God," because we introduced him to the Deity in a flowing beard and frock coat.

"The atom" is being widely exploited as the key to the power of the future. In a sense this may be correct, of course. But to give the idea real meaning and substance we cannot let the mere catch phrase suffice. In a similar sense, "the molecule" could be held responsible for much of the power of the present, but, perhaps unfortunately, "Molly" never had so many willing press agents as has "Tommy the At." Nevertheless, the cracking, splitting, amputation, patching, and grafting which "the molecule" undergoes in modern petroleum technology makes the neuclear formation and disruption of plutonium seem child's play. And how about giving "the molecule" his due in the evaporation of water and the expansion of steam?

Sometime, I propose to vaunt the importance of the atom over that of the molecule, but that is another story. Meanwhile, let us try to keep these things in their proper perspective.

EARLY in September your Editor makes a move, trading the rock-bound coast of New England for the sandy beaches of southern California. Thenceforth, all editorial mail should be addressed to him at:

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More frequent use of the air mail service will keep him just as much "in the center of things" as ever. To his many friends in the East, whom he will not see as often in the future as in the past, he says "au revoir" but not "adieu."

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The Introduction to Thermodynamics[1]

DUNCAN MacRAE

Chemical Warfare Service, Edgewood Arsenal, Maryland

IT SOMETIMES happens in the development of the sciences that subjects are at first presented in such a way that they seem to have little relation to the other parts of the science to which they belong or to that science as a whole. This has resulted in delay in the acceptance of these subjects and in continued difficulty to both teacher and student until better methods of presentation have been devised. There is perhaps no better example of such a case than one in the field of mathematics given by J. Willard Gibbs. No knowledge of mathematics is required to understand his analysis of the difficulty in this case and the nature of the remedy which he offered in his pamphlet on "Vector Analysis."

In defending this pamphlet[2] against the criticisms of the quaternionists, he began by stating with great certainty that the "*first* duty of the physical vector analyst *qua* physical vector analyst . . . is to present the subject in such a form as to be most easily acquired, and most useful when acquired." This was in reply to a question by Mr. McAulay. He then quoted him as follows:

> Quaternions differ in an important respect from other branches of mathematics that are studied by mathematicians after they have in the course of years of hard labor laid the foundation of all their future work. In nearly all cases these branches are very properly so called. They each grow out of a definite spot of the main tree of mathematics, and derive their sustenance from the sap of the trunk as a whole. But not so with quaternions. To let these grow in the brain of a mathematician, he must start from the seed as with the rest of his mathematics regarded as a whole. He cannot graft them on his already flourishing tree, for they will die there. They are independent plants that require separate sowing and the consequent careful tending.

He then went on to say:

> Can we wonder that mathematicians, physicists, astronomers, and geometers feel some doubt as to the value or necessity of something so separate from all other branches of learning? Can that be a natural treatment of the subject which has no relations to any other method, and as one might suppose from reading some treatises, has only occured to a single man? Or, at best, is it not discouraging to be told that in order to use the quaternionic method, one must give up the progress which he has already made in pursuit of his favorite science, and go back to the beginning and start anew on a parallel course?
>
> I believe, however, that if what I have quoted is true of vector methods, it is because there is something fundamentally wrong in the presentation of the subject. . . .
>
> If I wished to attract the student of any of these sciences to an algebra for vectors, I should tell him that the fundamental notions of this algebra were exactly those with which he was daily conversant. . . .

Gibbs expressed these views some 15 years after the publication of the last of his three great papers on thermodynamics. Yet it did not seem to occur to him that what he said of quaternions and mathematics applied equally well to thermodynamics and physics. How different the history of science might have been if he had practiced, with respect to thermodynamics and physics, the principles of presentation which he thus set forth 15 years later in connection with vector analysis and mathematics!

The early history of the presentation of thermodynamics as it actually was has been given by Lewis and Randall:[3]

> The second law of thermodynamics, which is known also as the law of the dissipation or degradation of energy or the law of the increase of entropy, was developed almost simultaneously with the first law through the fundamental work of Carnot, Clausius, and Kelvin. But it met with a different fate, for it seemed in no recognizable way to accord with existing thought and prejudice. The various laws of conservation had been foreshadowed long before their acceptance into the body of scientific thought. The second law came as a new thing, alien to traditional thought, with far-reaching implications in general cosmology.
>
> Because the second law seemed alien to the intuition, and even abhorrent to the philosophy of the times, many attempts were made to find exceptions to this law, and thus to disprove its universal validity. But such attempts have served rather to convince the incredulous, and to establish the second law of thermodynamics as one of the foundations of modern science. In this process we have become reconciled to its philosophical implications, or have learned to interpret them to our satisfaction, we have learned its limitations, or better, we have learned to state the law in such a form that these limitations appear no longer to exist; and especially we have learned its correlation with other familiar concepts, so that it now no longer stands as a thing apart; but rather as a natural consequence of long familiar ideas.

There is no question that in the 73 years which elapsed between the announcement of the second law and the publication of Lewis and Randall's book on "Thermodynamics" there was a tremendous improvement in the presentation and acceptance of the second law. In the 23 years since its publication there has been a still further improvement in that respect, and it is generally conceded that their book played a great part in the advancement of the subject; but it should not be concluded that there is now no need for further improvement in the presentation of the subject. Within recent years there have been a number of articles published on the teaching of thermodynamics, and some excellent textbooks have been published. It appears from the attention which is being given to it that the

[1] Presented before the Division of Chemical Education at the 109th meeting of the American Chemical Society in Atlantic City, April 8–12, 1946.

[2] GIBBS, J. W., *Nature*, **47**, 463–4 (1893); "Collected Works," Longmans, Green, and Company, New York, **1931**, Vol. II, pp. 169–72.

[3] LEWIS, G. N., AND M. RANDALL, "Thermodynamics," McGraw-Hill Book Company, New York, 1st Ed., **1923**, pp. 109–10.

student has even now more than a reasonable amount of difficulty with the subject.

Let us inquire briefly as to the extent and nature of this difficulty. R. H. Wright[4] says:

> There can be little doubt that the Second Law of Thermodynamics is one of the major hurdles in the path of most students of physical and theoretical chemistry. Far too many undergraduates never perceive what the Second Law is or how it came to be formulated, even though they may acquire some facility in the use of thermodynamic formulas for solving routine problems.

Nor is the difficulty limited to undergraduates. When so eminent a thermodynamicist as Professor Brönsted[5] "asserts that the concepts of traditional thermodynamics are characterized by a lack of clarity, that they result in incompleteness and awkwardness of treatment, and that they unavoidably lead to contradiction," and when another eminent thermodynamicist, Professor MacDougall, is of the opinion that "such conclusions can result only from a complete misunderstanding of the concepts employed in traditional thermodynamics" and implies that most chemists and physicists have similar troubles, it will be difficult to dismiss the situation as too trivial to warrant further consideration. MacDougall's remarks in this connection so well illustrate the conflict between the concepts of thermodynamics and those which the student has just been at great pains to acquire in elementary physics that they are quoted fully below:

> As might be expected, difficulty arises in connection with the concepts of heat and work. It is an unfortunate fact that most chemists and physicists in thermodynamic discussions often make use of expressions, borrowed perhaps from other fields of science, which are inaccurate or misleading if they are regarded as thermodynamic statements. The familiar remark that work done against frictional forces is converted into heat is an example of a misleading phrase. In classical thermodynamics no attempt is made, nor is it considered useful, to subdivide the energy of a body into various forms, such as the kinetic energy of translation and of rotation of the molecules and the kinetic and potential energies of atomic vibrations, although this procedure is highly desirable when studying the body from the standpoint of the kinetic theory and statistical mechanics.
>
> When two systems A and B are in contact, there may be a transfer of energy from one system to the other in one or more ways. For example, matter (containing energy) may pass from A to B, or energy unaccompanied by matter may flow from A to B. In the latter case we speak of a transfer of heat or of work or of both, depending on the nature and the observed behavior of the two systems. If the transfer of energy from A to B is due solely to the fact that the temperature of A is higher (even infinitesimally higher) than that of B, then we say that energy in the form of heat has passed from A to B. Strictly speaking, it is only in the moment of its passing from A to B that the energy being transferred is called heat. We do not say that the energy was heat while it was in the system A nor after it is added to the energy originally in B.
>
> Similarly, if a set of weights on a piston brings about a compression of a gas, we say that the weights and the piston have done mechanical work on the gas or that energy has been transferred from the weights and piston to the gas in the form of work. We should not, however, say that the amount of work in the gas has been increased and that the amount of work possessed by the weights and the piston has been diminished, unless we are prepared to give the term "work" some new meaning. In the same way, it is not allowed to speak of the quantity of heat in a system unless some additional, properly defined significance is given to the term "heat."

These quotations from Wright and MacDougall show that the difficulty is not confined to a few beginners.

Perhaps MacDougall has indicated the real cause of the trouble when he said that "expressions, borrowed perhaps from other fields of science, . . . are inaccurate or misleading if they are regarded as thermodynamic statements." The examples given by him in this connection relate to subjects which the beginning student has just studied for two years in high-school and college physics. For certain thermodynamic purposes the student must put aside nearly all that he has learned about heat and must resolutely remember "that heat exists only when it flows." Similarly, much of what he has learned about energy must be put aside as either useless or positively harmful. He will hear no more of kinetic and potential energy for a long time, unless he is taught by a chemical engineer.[6] In that case he will see kinetic, potential, and internal energy side by side in the same equation when Bernouilli's mechanical-energy balance is used as a basis for the study of fluid flow. Otherwise, he may never hear of kinetic energy and will not meet his old acquaintance, (gravitational) potential energy, until he nears the end of an advanced course in thermodynamics. This should be strange to a student who first learned about energy from simple illustrations involving the lifting of a weight from one gravitational potential to another. Further, some authors would have him forget that he ever learned that energy is defined as "capacity for doing work." Although the student has learned to define, measure, and use gravitational and electrical potentials together with appropriate related quantities[7] in calculations involving energy and work, the relation between temperature and these other potentials is seldom, if ever, pointed out. (It is true that this might well be done in high-school or college physics.) From the introduction of the subject of temperature as given in some texts on thermodynamics it might be thought that the student has learned nothing useful about temperature since grammar school. Nor is the similarity between chemical potentials and the other potentials fully utilized in presenting the subject. Then too, a great emphasis on the first and second laws and a tendency to regard heat as unique with respect to its convertibility into work have both contributed to the profound lack of symmetry in the presentation of thermodynamics and that of the other branches of energetics treated in elementary physics. This lack of symmetry is the more unfortunate because it does not seem to be necessary, but seems

[4] WRIGHT, R. H., J. CHEM. EDUC., **18**, 263–9 (1941).

[5] MACDOUGALL, F. H., *J. Phys. Chem.*, **44**, 713–5 (1944).

[6] COMINGS, E. W., J. CHEM. EDUC., **16**, 312–4 (1939).

[7] These potentials and quantities are not always the same as the "intensity and capacity factors of energy" listed by Getman and Daniels in the seventh edition of their "Physical Chemistry," as will be seen from the fact that they list heat capacity as the factor corresponding to difference in temperature. Nor are they the same as the "intensive and extensive variables" mentioned in MacDougall in the revised edition of his "Physical Chemistry."

to result from an arbitrary or accidental emphasis on the differences between thermodynamics and these other subjects rather than on their similarities. The student may well have his doubts as to "the value or necessity of something so separate from all other branches of learning."

If, then, there is something fundamentally wrong in the presentation of beginning thermodynamics and if the difficulty largely consists of a failure to relate the subject matter of thermodynamics to the other branches of energetics recently studied in physics, we may owe a great debt to Brönsted[8] for writing a paper showing a different method of introducing the subject, for his method seems to be capable of better relating the subject of thermodynamics to the other branches of energetics and to the science of physics as a whole. It is, of course, not necessary to accept all that Brönsted says in these two papers. MacDougall's potent comments on one of them have been extensively quoted above. Both articles are also discussed by Boris Leaf in a very interesting paper.[9]

Whatever may be the faults of these two papers by Brönsted, they do contain one idea which seems to be well adapted to use in presenting the subject matter of thermodynamics to students who have recently finished college physics. Such students would be familiar with many examples of at least three types of Brönsted's "basic energetic process." In the operation of a water motor or pump this process consists of the flow of a weight (quantity) of water from one height (gravitational potential) to another; or in the same apparatus it may consist of the flow of a volume of water from one pressure to another. In that case the volume is the quantity and the pressure is the potential. In the operation of an electrical motor or generator, the process consists of the flow of a quantity of electricity from one electric potential to another.

In considering such processes, the student has made numerous applications of the equation

$$-W_r = (P_2 - P_1)\Delta K \qquad (1)$$

in which $-W_r$ is the lower limit of the work required to transfer some quantity,[10] ΔK, from a potential P_1 to a potential P_2. Also, $+W_r$ is the upper limit of the work obtainable when the quantity is transferred from the higher to the lower potential. He already knows that these two limits are numerically equal to each other and could be shown without too great difficulty that they are equal to the work obtained in a reversible process. Early in the study of mechanics in high school[11] he learned that "if we lift 100 pounds 3 feet, we do 300 foot-pounds of work." Later, he learned that "if a water motor attached to a faucet uses 4 cubic feet of water per minute and the pressure gage shows a pressure of 50 pounds per square inch," the upper limit of the work obtainable in that time from any such motor is $4 \times 50 \times 144$, or 28,800 foot-pounds. Also, while he was still in high school, he learned that the work obtainable from an electric motor or generator is the product of the quantity of electricity flowing through it multiplied by the difference in potential across its terminals. For example, he has calculated that a generator supplying 40 amp. at 500 volts would generate 20 kw. of power or 40 amp. $\times$ 3600 sec. $\times$ 500 v. = 144,000 coulombs $\times$ 500 v. = 72,000,000 joules of energy per hour capable of doing $72{,}000{,}000 \times 0.0738 = 53{,}136{,}000$ ft.-lb. of work per hour.

In college he learned to define the unit of electric charge as follows: "One coulomb is the amount of electric charge that requires one joule of energy to move it through an opposing potential difference of one volt." This definition is, of course, a verbal statement of equation (1) above. In these applications the energetic quantities are weight,[12] volume, and electric charge, and the corresponding potentials are height, pressure, and electrical potential, respectively.

Nor does this by any means exhaust the student's knowledge of applications of equation (1). The definition of energy which he learned in high school can be developed, with the aid of the law of the conservation of energy and the old familiar illustrations of elementary physics, into a form more suitable for use in thermodynamics. Let us consider a process which consists of the pumping of 100 lb. of water from a reservoir at 20 ft. above sea level to one at 120 ft. If we call its energy in the initial state E_1 and its final state E_2, the increase in the energy of the 100 lb. of water will be

$$\Delta E = E_2 - E_1 \qquad (2)$$

The student has already learned how to calculate potential energy and, probably without hesitation, would place

$$\begin{aligned} \Delta E &= 100 \times 100 = 10{,}000 \text{ ft.-lb.} \\ E_2 &= 100 \times 120 = 12{,}000 \text{ ft.-lb.} \\ E_1 &= 100 \times 20 = 2000 \text{ ft.-lb.} \end{aligned}$$

It should be pointed out to him, however, that these cal-

[8] BRÖNSTED, J. N., *Phil. Mag.*, **29**, 447–70 (1940); *J. Phys. Chem.*, **44**, 699–712 (1940).

[9] LEAF, B., *J. Chem. Phys.*, **12**, 89–98 (1944).

[10] The student may wonder why this quantity is designated as an increment rather than by a single letter. For purposes which will be apparent later, it is convenient to consider the basic process to consist of the flow of the quantity from a reservoir at a potential P_1 to another reservoir at a potential P_2. In such cases ΔK will not only represent the magnitude of the quantity flowing through the machine, but $-\Delta K$ will also represent the decrease in the quantity in one reservoir and $+\Delta K$ the increase in the quantity in the other. It may be considered that in using this notation, the student's attention is being called to a difference in point of view of the chemist and physicist with regard to thermodynamics. The physicist and the engineer are interested in the machine and the work done by it. The chemist, however, is interested primarily in changes in the substances in the reservoirs when the various energetic quantities are added to or withdrawn from them.

[11] Statements in this paper as to what the student has learned in high school are largely based on the text of "New Practical Physics" by N. H. BLACK AND H. N. DAVIS, published by the Macmillan Company, New York, 1933. Similarly, information as to college physics is based on "Matter, Motion, and Electricity" by H. D. SMYTH AND C. W. UFFORD, published by the McGraw-Hill Book Company, New York and London, 1939.

[12] Weight and height can, of course, be used in this connection only when weight does not change appreciably with height. When this is not the case, mass and gravitational potential must be substituted for them.

culations are based on a number of assumptions. In making the first calculation he has tacitly assumed that the increase in energy of the 100 lb. of water is equal to the work done when it is lifted 100 ft. by a reversible process—that is,

$$\Delta E = W, \tag{3}$$

This is equivalent to the assumption that, during the process, no other energy, either in the form of heat or work, is received by the water from its surroundings. It follows from equation (1) that

$$\Delta E = (P_2 - P_1)\Delta K \tag{4}$$

The first calculation was equivalent to the use of equation (4). In making the other two calculations he has assumed that the total energy of the 100 lb. of water at the height, P, is equal to the work required to lift it from sea level to that height, or

$$E = P\Delta K \tag{5}$$

In all three calculations the student has confined his attention to a system consisting of 100 lb. of water rather than to the changes in the quantities of water in the two reservoirs. Accordingly, for his purposes, it would seem more natural to replace ΔK in all the above equations by K. We would then have for equation (5),

$$E = PK \tag{6}$$

If, however, he were considering the increase in energy of the top reservoir when the amount of water in it is increased by 100 lb. without changing its level, the following notation would perhaps be more suitable to represent the relation involved:

$$\Delta E = P\Delta K \tag{7}$$

If the level of the water in the reservoir is not held constant but the quantity of water added is so small that it does not appreciably change the level of the water in the reservoir, equation (7) becomes

$$dE = PdK \tag{8}$$

In all of the above applications of equations (1), (2), and (3) to energy changes when weights are lifted from one level to another, it has been assumed that the energy of the systems considered has been completely determined by their weight and height as stated by equation (6). This has caused no difficulty in the cases considered because any changes in energy caused by changes in volume, electric charge, or any other energetic quantity have been negligible, and because it has made no difference what absolute values were assigned to the total energies of the systems considered. The fact that equation (8) holds only under these conditions is expressed by putting it in the form

$$\partial E/\partial K = P \tag{9}$$

In all the other equations given above there is no notation suggesting the constancy of the other variables affecting the value of the energy.

Equation (9) is of especial interest for two reasons. First, if P represents any potential and K its corresponding energetic quantity, equation (9) is a definition of any potential. The student may be surprised to learn that height above sea level can be defined as the partial derivative of energy with respect to the weight of water in a reservoir. This is, however, equivalent to saying that, when 1 lb. of water is added to a reservoir, its energy, expressed in foot-pounds, increases by an amount equal to its height above sea level. This is not surprising when it is remembered that the potential energy of one pound of water is numerically equal to its height above sea level. Also, if the energy of a body is a function of several energetic quantities, K_1, K_2, and K_3, such as its weight, volume, and electric charge, this fact can be expressed by the equation

$$dE = \frac{\partial E}{\partial K_1} dK_1 + \frac{\partial E}{\partial K_2} dK_2 + \frac{\partial E}{\partial K_3} dK_3 \tag{10}$$

and it follows from equation (9) that for a reversible process

$$dE = P_1 dK_1 + P_2 dK_2 + P_3 dK_3 \tag{11}$$

Each of the terms in the right-hand member of the equation corresponds to a method of adding energy to the system under consideration. It will be observed that, in general, the energy of the system increases when any of its energetic quantities increase. For example, when the volume of a quantity of gas is increased by adding an infinitesimal quantity of the same gas at the same pressure, its energy increases. But if its volume increases by allowing the gas to expand and do work on the surroundings, without doing any other kind of work or absorbing any heat, the energy of the gas decreases. This is indicated by the usual minus sign before the appropriate PdK (*i. e.*, pdv) term. The question of adding terms to equations (10) and (11) to represent the change in energy when heat flows into the system or when substances capable of reacting chemically are added must be deferred until later.

The student should also have his attention called to the fact that his calculations have assumed that the change in energy of a system depends solely on the initial and final states of the system; or "(1) the energy of a system is a single-valued function of the variables which determine the thermodynamic state of a system, (2) the difference in energy of a system in two states is a function of these states only, (3) the change in energy of a system in a cyclic process is zero, and (4) the element of energy, dE, is an exact differential. Any one of these four statements is a formulation of the first law of thermodynamics."[13] Another form of the first law may be given the student at this point. It is somewhat ponderous but seems to have much in common with the student's first introduction to the law of the conservation of energy in high school. Planck[14] says:

The first law of thermodynamics is no other than the universal Principle of Conservation of Energy applied to heat processes.

[13] MACDOUGALL, F. H., "Thermodynamics and Chemistry," John Wiley and Sons, New York, 3rd Ed., 1939, p. 45.

[14] PLANCK, M., "Theory of Heat," The Macmillan Company, London, 1932, p. 28.

The energy E of a physical configuration may be regarded as a capacity to do work which is conditioned and uniquely determined by the momentary state of the configuration and which can occur in various forms and undergo various transformations but, so long as the configuration is isolated from the exterior, is of definite amount which does not vary with respect to the time. Thus, E = a constant or $E - E' = 0$, if E refers to the initial state and E' to the final state of the configuration.

Compare this statement with the following from Black and Davis:[15]

Thus, in the pendulum the sum of the kinetic and potential energies is the same wherever it is in its swing unless there is friction. If there is friction, some energy disappears as heat and less is left in the pendulum, but the total energy is unchanged.

We have but a step further to go in this direction to show the student how kinetic, potential, and internal energies are combined in Bernouilli's mechanical-energy balance. A few quantitative problems relating to the flow of fluids through orifices would do a chemist no harm and might help to bridge the gap between physics and chemical thermodynamics. An important case in the treatment of such problems is that in which the fluid under consideration neither gains nor loses energy in the process considered. In the usual analytical statement of the first law of thermodynamics we have

$$\Delta E = Q - W \quad \text{or} \quad dE = Q - W \qquad (12)$$

in which Q is the heat absorbed and W is the work done by the system. It is in connection with this equation that the student must remember that heat does not exist except when it flows. Since $-W$ is the work done on the system, this equation says that the increase in energy of a system is equal to the energy added to it. If no energy is added (or lost), the sum of the various forms of energy for the final state is the same as that for the initial state, and valuable information may sometimes be obtained by equating the two sums.

In chemical thermodynamics, it is the usual practice to deal with systems at rest and constant height above sea level. This excludes the necessity for consideration of kinetic and potential energy. Consequently, E is considered to be the internal energy of the system. In so doing we should not lose sight of the fact that equation (12) holds even if E should represent the total energy of the system. This is also true of equation (2).

Equations (2) and (12) are not only so general that they may include both kinetic and potential energy, but they are also more general in another respect than any of the equations so far presented. They apply to both reversible and irreversible processes. Also equation (12) makes specific reference to the increase in energy of a system by the absorption of heat, a process which has not previously been considered in this paper. For a reversible process, equation (12) can be written

$$\Delta E = Q_r - W_r \quad \text{or} \quad dE = Q_r - W_r \qquad (13)$$

When no heat is absorbed, equation (13) becomes equation (3). Under the same condition, it is equivalent to equation (11) provided the PdK terms include all the potentials and quantities involved in the work done on the system.

Since the matter of distinction between heat and the flow of heat has been the cause of so much trouble, it may be well worth while to attempt to clarify it with an illustration such as might have been given in high-school physics. Let us return to the consideration of the 100 lb. of water in a reservoir 100 ft. above another reservoir. It can be considered to have 10,000 ft.-lb. of potential energy with respect to the lower reservoir. The student knows that it is theoretically possible with a perfect machine and very great care to obtain 10,000 ft.-lb. of work when the 100 lb. of water flows from one reservoir to the other. He also knows that with any practicable operation of any real water motor, he will obtain only a fraction of the potential energy in the form of work. He still further knows that the water can flow from one reservoir to the other without doing any work. In that case he will probably believe that all of the potential energy appears in the surroundings or the water itself as heat. But suppose the water flows through a capillary so that it does no work and emerges at the lower reservoir with so small a velocity that its kinetic energy is negligible. And suppose that conditions are such that no heat is lost to the surroundings. Such conditions could probably be approximated with thick-walled glass capillary tubing after a preliminary flow of water for some time from one reservoir to another. Applying equation (12) under these conditions, we find that no work was done and no heat was absorbed, so there was no change in the total energy of the water. But the student may possibly say that there was a "loss in gravitational potential energy" and a "gain in heat" by the water. He can point to his calculations as evidence of his first contention and to the rise in temperature of the water as evidence of the second. It will be consistent with this evidence and his previous instruction to say that potential energy has been converted into heat. The case is not unlike that of the pendulum mentioned above in which kinetic and potential energy were constantly being converted into each other, but the total energy of the pendulum could not change unless energy in some form entered the pendulum from its surroundings or passed from the pendulum to the surroundings. These two examples emphasize the points that in equation (12) ΔE is the change in the energy of the system and Q is the heat which flows into or out of the system, and W is the work done *on* or *by* the system *during* the change in state under consideration. If at the end of the process the water had been cooled to its initial temperature, it would follow from equation (12) that the energy had decreased in that process by an amount equal to the energy lost in the flow of heat to the surroundings. If now we consider the over-all change in state resulting from the two processes of flow and cooling, we find that the initial and final states of the water differ only in the magnitude of the gravitational potential or height above sea level. Consequently, no energetic quantities or

[15] BLACK, N. H., AND H. N. DAVIS, *Loc cit.*, p. 198.

potentials other than weight and height are involved and equation (4) can be used to calculate the loss in total energy in the change in state under consideration. Accordingly, since the loss in potential energy and the heat lost to the surroundings are each equal to the decrease in total energy, they are equal to each other. Thus, equations (4) and (12) lead to the conclusion that a quantity of potential energy has been converted into an equivalent *flow* of heat to the surroundings.

While still in high school the student was taught "that in order to get water to flow along a pipe, it is essential to have some driving force furnished either by a difference in water level or by a pump. In much the same way, to get electricity to flow along a wire, we must have electromotive force, such as that furnished by the difference of potential of an electric cell or some other electric generator. . . . Electromotive force (abbreviated e. m. f.) is sometimes called 'voltage' or 'difference of potential.' All these terms refer to the same thing—namely, the 'push' that moves or tends to move electricity." In college physics he has gone into the subject of electric potential still further.[16] The analogy between gravitational and electrical potential has been discussed and he has learned the definition: the difference in electrical potential between any two points is the energy per unit charge required to move a positive charge from one point to the other. The student will readily see that this is just another application of equation (1). If some potential, such as that of the earth or that of the hydrogen electrode, is arbitrarily selected as the standard or zero potential, we have a situation somewhat similar to that which led to equation (5), and equation (1) becomes

$$W_r = P\Delta K \quad \text{or} \quad P = W_r/\Delta K \tag{14}$$

With the aid of this equation, the electrical potential at a point can be defined as the energy per unit charge required to move a positive charge from a point of zero potential to the point in question.

When the student has reviewed his knowledge of potentials to this point, he might be led to inquire if there is not a chemical potential from which the tendency of a chemical substance to pass from one solution or compound to another might be predicted. If such potentials can be found, it might be possible to predict whether or not a given reaction would take place. They would be very useful, for it is one of the two[17] great problems of chemistry to make such predictions. Of course, vapor pressures and partial pressures and equilibrium constants are already useful in predicting the direction of chemical changes. If, for example, moist air is passed over a water surface at a given temperature, water vapor will pass from the water to the air or in the reverse direction, depending on whether the vapor pressure of the water is greater or less than the partial pressure of the water vapor in the air. Also, if the partial pressures of the reactants and products are specified for a proposed reaction and if the equilibrium constant for the reaction is known, it is frequently possible to predict whether the reaction can take place; for if we substitute the specified partial pressures for those in the expression for the equilibrium constant, the result will be either greater than, equal to, or less than the equilibrium constant. When it is less than the equilibrium constant, the reaction will take place.

This is all very well, but if we wish to use the same sort of methods in all different branches of energetics, there will be some advantages in the use of chemical potentials. If such potentials can be defined in the same way as gravitational and electrical potentials, we would have the following: The difference in chemical potential for any substance in two homogeneous masses is equal to the amount of mechanical work required to bring one mol of the substance by a reversible process from one mass to the other.[18] This assumes that no other energetic quantities or potentials are involved in the transfer. Or, if for each chemical substance we can adopt a standard reference state in which the chemical potential can arbitrarily be called zero, the above definition becomes: The chemical potential for any substance in a homogeneous mass is equal to the amount of mechanical work required to bring one mol of the substance by a reversible process from a state in which its chemical potential is zero into the homogeneous mass in question. In fact, it is common practice to take the chemical potential of the elements as zero in the pure state at 25°C. and 1 atm. pressure. Chemical potentials so defined determine the direction of chemical and physical changes in much the same way as do vapor pressures and partial pressures. If the chemical potential of water vapor in moist air, for example, is greater than that of liquid water, moisture would condense from the moist air to the water surface. If, on the other hand, the potential of the liquid water were the greater, the water would evaporate into the air. This, of course, applies to the direction of passage of water from any homogeneous mass or phase to another. Similar potentials exist for all other chemical substances. In applying these potentials to the prediction of the directions in which proposed chemical changes can take place, it is convenient first to calculate the potentials of the chemical elements in a gaseous mixture in equilibrium with a pure chemical compound. If, for example, we know the partial pressures of mercury and oxygen in equilibrium with solid mercuric oxide in dry nitrogen at 25°C. and 1 atm., we can calculate the potentials of these two elements in the nitrogen. From the definition of chemical potential given above it can be shown that

$$P = RT \ln p \tag{15}$$

in which P is the chemical potential of the elementary substance in question and p is its partial pressure (or,

[16] SMYTH, H. D., AND C. W. UFFORD, "Matter, Motion, and Electricity," McGraw-Hill Book Company, New York, 1939, chap. XI.

[17] The other has to do with the rate at which chemical changes take place and lies outside the scope of the present paper.

[18] This may be compared with the more exact and general definitions given by GIBBS, *loc cit.*, Vol. I, p. 95.

more exactly, its fugacity) in the equilibrium mixture. We next consider the chemical reaction by which the compound is formed from its elements and multiply the chemical potential of each element in equilibrium with the compound by the number of mols of the element in question required to form one mol of the compound. The sum of these products is called the free energy of the compound and is designated by the letter F. Now, for any definite proposed chemical change we can state the following rule: If the sum of the free energies of the reactants is greater than the sum of the free energies of the products, the reaction can take place spontaneously if a suitable catalyst is present. In applying this rule, it must be remembered that the free energy of each reactant or product is the free energy of one mol of the substance multiplied by the number of mols taking part in the reaction.

Having thus called the attention of the student to the need for an energetic potential with which he was not previously acquainted, his attention can now be well directed to the need for an energetic quantity closely related to heat. He knows that heat is a form of energy and that it is partly converted into work by means of steam engines and other heat engines. He has been told in high school that "in a modern steam plant, whether it be a locomotive, an ocean liner, or a central power station, the steam is made in a boiler, is used in a steam engine, and is usually discharged into the air or into a condenser." He can be shown that discharge of steam into the air at 1 atm. is equivalent to its discharge into a condenser at 100°C., for in each case the pressure is 1 atm. It has even been suggested vaguely that the work obtained from the steam engine is greater the greater the difference in temperature between the boiler and the condenser. If the student were asked to apply equation (1) to the calculation of the work obtainable from a steam engine, he would probably select heat as the proper energetic quantity to be multiplied by the thermodynamic temperature difference. It would then be necessary to point out that the result so obtained is not satisfactory because it is not in units of work. It could be further pointed out that the quantity of heat which flows into the condenser cooling water would be less than that which flowed into the boiler and that the difference was equal to the amount of work performed by the steam engine, so he must look for some quantity other than heat to use in the desired calculations.

When we find this quantity, we may expect from equation (1) that we can define the thermodynamic temperature scale as simply as we now define other potentials—that is to say, the difference $(T_1 - T_2)$ between any two temperatures will be equal to the energy required to transfer a unit of the new quantity from the lower to the higher temperature, *e. g.*, by means of a perfect refrigerating machine. The new quantity will be expressed in units of calories per degree and, unlike heat, will remain unchanged in amount when it is transferred from one temperature to another by a reversible process. It will be shown that it is simply related to a property of substances invented nearly 100 years ago. This property is called the entropy, S, and is defined by the statement that the increase in the entropy of a body during an infinitesimal stage of a *reversible* process is equal to the infinitesimal amount of heat absorbed divided by the absolute temperature of the body.[19]

In symbols, this is:

$$dS = dQ/T \text{ (for a reversible process)} \qquad (16)$$

This equation does not hold for irreversible processes. For example, it might be hastily concluded that if no heat is absorbed in a process, there is no change in the entropy of the substance involved. A gas may expand into a vacuum in such a way that no heat is absorbed or given out. This, however, is an irreversible process. The entropy change in the process can be found by considering a reversible process with exactly the same initial and final states as the one in question. In that case the gas would absorb heat at constant temperature, and ΔS would equal Q/T. For other processes like the vaporization or condensation of water taking place at *constant temperature* and very nearly under equilibrium conditions, the increase in entropy, ΔS, is also equal to Q/T. The entropies of vaporization of liquids are thus calculated with great ease from their heats of vaporization and their boiling points on the thermodynamic temperature scale. Trouton's rule states that the molal entropy of vaporization for many liquids is approximately equal to 20 entropy units.

With this definition we have found the term to be added to equations (10) and (11) to represent the gain of energy in the form of heat, for temperature is the potential and entropy is the energetic quantity required. Further, Gibbs, in giving a geometrical expression of the second law of thermodynamics, indicates that equation (16) is the analytical expression of that law and, in addition, shows us the quantity required for the application of equation (1) above to calculate the work obtainable from heat engines. The following quotation not only contains that geometrical expression of the second law but also is notable for the views it expresses on the teaching of thermodynamics to the beginner:

> It is worthy of notice that the simplest form of a perfect thermodynamic engine, so often described in treatises on thermodynamics, is represented in the entropy-temperature diagram by a figure of extreme simplicity, *viz.*, a rectangle of which the sides are parallel to the coordinate axes. Thus in the figure the circuit *ABCD* may represent the series of states through which the fluid is made to pass in such an engine, the included area representing the work done, while the area *ABFE* represents the heat received from the heater at the highest temperature *AE*, and the area *CDEF* represents the heat transmitted to the cooler at the lowest temperature *DE*. . . .
>
> It is often a matter of the first importance in the study of any thermodynamic engine to compare it with a perfect engine. Such a comparison will obviously be much facilitated by the use of a method in which the perfect engine is represented by such simple forms.
>
> The method in which the coordinates represent volume and pressure has a certain advantage in the elementary character of

[19] MACDOUGALL, F. H., "Physical Chemistry," The Macmillan Company, New York, 1943, p. 216.

the notions upon which it is based, and its analogy with Watt's indicator has doubtless contributed to render it popular. On the other hand, a method involving the notion of *entropy*, the very existence of which depends upon the second law of thermodynamics, will doubtless seem to many far-fetched and may repel beginners as obscure and difficult of comprehension. This inconvenience is perhaps more than counterbalanced by the advantages of a method which makes the second law of thermodynamics so prominent and gives it so clear and elementary an expression. The fact that the different states of a fluid can be represented by the positions of a point in a plane so that the ordinates shall represent the temperatures, and the heat received or given out by the fluid shall be represented by the area bounded by the line representing the states through which the body passes, the ordinates drawn through the extreme points of this line and the axis of abscissas—this fact, clumsy as its expression in words may be, is one which presents a clear image to the eye and which the mind can readily grasp and retain. It is, however, nothing more or less than a geometrical expression of the second law of thermodynamics in its application to fluids in a form exceedingly convenient for use and from which the analytical expression of the same law can, if desired, be at once obtained. If, then, it is more important for purposes of instruction and the like to familiarize the student with the second law than to defer its statement as long as possible, the use of the entropy-temperature diagram may serve a useful purpose in the popularizing of this science.

From the diagram it is evident that the analytical expression of the second law is

$$dQ = TdS \text{ (for reversible processes)} \qquad (17)$$

Consequently, if we call the higher temperature indicated on the diagram T_1 and the lower temperature T_2 and if the increase in entropy along the line AB is called ΔS, the heat received at the higher temperature will be $T_1\Delta S$ and that transmitted to the cooler at the lower temperature will be $T_2\Delta S$. Also, the work done will be given by the equation.

$$W_r = \Delta S(T_1 - T_2) \qquad (18)$$

This equation is just another application of the more general equation (1). In it, S is the quantity we have been seeking. In calculating the work obtainable in a perfect heat engine, all that we have to do is multiply the difference between the temperature of the heater and that of the cooler by the entropy lost by the heater. If the heater is maintained at constant temperature, the entropy lost will be the quantity of heat which flowed out of it divided by the absolute temperature. When such a quantity is multiplied by the difference in temperature, the result obtained is expressed in energy units and not in energy units multiplied by temperature units as was the case when the quantity of heat supplied by the heater was multiplied by the difference in temperature. Further, it is seen from the diagram that the quantity of entropy lost by the heater is the same as that gained by the cooler. This avoids the second objection to heat as the energetic quantity to be used with the potential, temperature. We are also in a position now to define temperature in the same manner as other potentials as follows: The temperature of a substance is equal to the work required to transfer a unit quantity of entropy from zero thermodynamic temperature to the temperature of the substance. Temperature may also be defined as the increase in energy of the substance when a unit of entropy is added to it at that temperature when all other energetic quantities and potentials are held constant. In this way we can show the student certain similarities between thermodynamics and other branches of energetics.

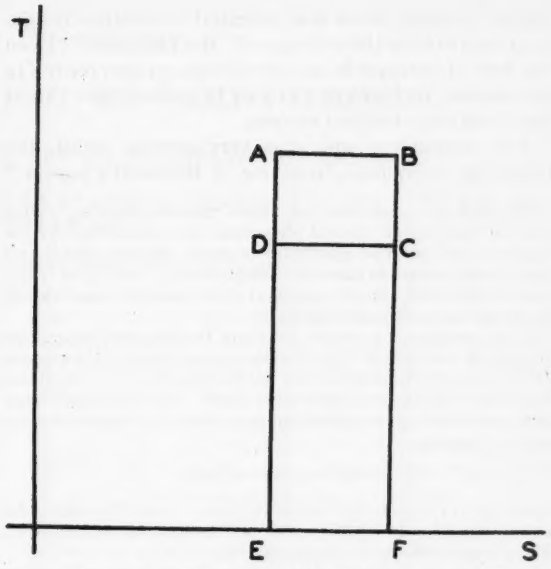

FIGURE 3 FROM PAGE 10 OF VOLUME I, "THE COLLECTED WORKS OF J. WILLARD GIBBS"

We have seen above that the amount of work obtainable from the flow of a quantity of entropy from the temperature T_1 to the temperature T_2 is given by equation (18). This is, of course, for a completely reversible process. It should be profitable to see what happens when a quantity of entropy flows from one temperature to another by a completely irreversible process in which no work is done. But let us first consider the analogous cases when other energetic quantities flow from one potential to another without doing any work. In the case of the flow of water through a capillary tube described above, we saw that the decrease in energy of the system could be calculated with the aid of equation (4) and from the loss of energy in the form of heat to the surroundings. By the law of the conservation of energy these two were equal. Similarly, when a charge of electricity flows through a wire from one electrical potential to another, it is well known that the quantity of heat which flows from the wire to the surroundings is equal to the amount of work which could have been produced when the same change took place by a reversible process and hence could be calculated by equation (1). This is also true when entropy flows from a place of one temperature to one of another through a conductor so we can consider that the amount of heat which flows into the surroundings is given by equation (1) or (18). In every case if the surroundings were at constant temperature, the amount of entropy gained by the surroundings would be equal to the heat received by the surroundings divided by their temperature. Thus we see that in irreversible processes the flow of an en-

ergetic quantity from one potential to another results in an increase in the entropy of "the universe." Even the flow of entropy in an irreversible process results in an increase in entropy. It can be shown that this is true even in an isolated system.

For comparison with this very general result, the following are quoted from one of Brönsted's papers:[20]

> We shall now generalize the above considerations by stating that all macroscopic natural phenomena are conditioned by the transport of energetic quantities between different states and that in the reversible case the changes consist entirely of transports of this kind. Such a transport of an energetic quantity will be termed a basic energetic process. . . .
>
> It is possible to associate with any fundamental process an amount of work which is by definition proportional to the amount of the quantity transported and which depends on the two states between which the transport takes place. The work for a basic process between given initial and final states can thus be defined by the equation
>
> $$\delta A = (P_1 - P_2)\delta K$$
>
> where δK is the quantity transported and P_1 and P_2 magnitudes which depend only on the initial and final states, respectively. These magnitudes we shall call potentials.

It has been the principal object of this paper to show that this definition and equation can be of material assistance in utilizing the knowledge already acquired by the beginning student of thermodynamics to give him a good grasp of the new subject. Incidentally it has been shown that the analytical expression of the second law is a special case of the equation above taken from Brönsted.

Let us now compare the above statements with that of the second law attributed to Planck by Noyes and Sherrill:[21] "A process whose final result is only a transformation of heat into work is an impossibility." It seems that Brönsted has in effect extended this definition to read: A process whose final result is only the transformation of *energy* into work is an impossibility. Indeed he has gone further than this, so that now we can say: The transformation of *energy* into work is always associated with the transport of some energetic quantity from one potential to another.

In the above discussion entropy has been defined in the language of classical thermodynamics and in the words of Gibbs and of its modern champion, MacDougall. In addition, emphasis has been placed on an aspect of entropy recently discussed by Brönsted but not commonly presented to beginning students of thermodynamics.[22] This is that entropy flows and is conserved in reversible processes. It is just as important that the student be acquainted with the fact that entropy increases in irreversible processes and that heat is conserved in completely irreversible processes. It is also important that the student learn about entropy from statistical mechanics and that he learn to think of it as a measure of the randomness of a system. In the long run, none of these aspects should be emphasized to the exclusion of others. Consideration of the flow and conservation of entropy in reversible processes, however, does seem to be helpful in introducing the subject, for this aspect seems to be, more than any other, closely related to the student's previous knowledge of physics.

[20] BRÖNSTED, J. N., *Phil. Mag.*, **29**, 447–70 (1940).

[21] NOYES, A. A., AND M. S. SHERRILL, "A Course of Study in Chemical Principles," The Macmillan Company, New York, 2nd Ed., 1938.

[22] In fact, some objections have been raised to the assumption that there is such an aspect. In emphasizing the part played by entropy in irreversible processes, KARL K. DARROW, in a paper on "The concept of entropy" published in *Am. J. Phys.*, **12**, 183–96 (1944), concludes that we are forbidden from "imagining entropy as a substance, or a fluid, or anything that is conserved" and states that, "entropy does not obey a law of conservation, except, of course, in special cases." It is only in the special case of a completely reversible process that the conservation of entropy is considered in this report.

Meteorologists

The American Meteorological Society, through its President, Professor H. G. Houghton of the Massachusetts Institute of Technology, wishes to call to the attention of American colleges the fact that a large number of carefully selected college students were given training in professional meteorology at a few selected universities in this country, preparatory to their employment by the Army and Navy Meteorological Services. A number of these men before entering the meteorological field had done a considerable amount of graduate work in chemistry and chemical engineering and are now available for teaching and research in these fields.

In most of our colleges which offer nonprofessional courses in meteorology to meet the needs of students in geography, geology, and in agricultural subjects, it has been standard practice to have these nonprofessional courses taught by members of various departments. The return of many of the professionally trained service meteorologists offers an opportunity for our colleges to obtain the services of instructors who are capable of doing professional work in a chemistry or chemical engineering department and at the same time who are qualified as experienced and trained professional meteorologists to present stimulating nonprofessional courses in meteorology on a somewhat higher plane than may have been possible in the past.

The Society is anxious to cooperate with American colleges in providing information concerning these returning weather officers that might be helpful in placing them in suitable teaching positions. To that end, files have been kept which contain detailed information on the education and practical experience of these men. Inquiries may be directed to the Executive Secretary, American Meteorological Society, 5 Joy Street, Boston 8, Massachusetts.

A New System for the Classification of Compounds[1]

A Contribution from the Survey of Antimalarial Drugs[2]

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IN THIS paper are presented the details of a new system for the classification of compounds according to chemical structure. This system was evolved during the period 1942–45 when the Survey of Antimalarial Drugs, operating with funds allocated by the Office of Scientific Research and Development on recommendation by the Committee on Medical Research, was charged with the responsibility of organizing the pharmacological reports on those drugs which had been tested in a coordinated wartime antimalarial program. The system forms the basis for the arrangement of compounds in a forthcoming monograph, "A Survey of Antimalarial Drugs, 1941–1945."[3] The Survey system has marked advantages over other systems in current use and is capable of general application to compounds of known structure where the organization of a large number of such compounds presents a problem.

The scientific objective of the Survey of Antimalarial Drugs was to relate chemical structure and antimalarial activity; however, some form of organization of the compounds was required before any correlative studies could be started. The creation of a new classification system was undertaken only because of our conviction that all existing systems possessed such defects as to limit their usefulness seriously.

In our opinion any satisfactory comprehensive system for the classification of compounds must fulfill three main requirements. We set these requirements down in what we judge to be their relative importance.

Of primary importance—in fact, the only *absolute* requirement—is that there be a unique, predictable location in the system for every compound that can be adequately described. No other feature, however commendable, can substitute in whole or in part for this requirement, and any arrangement which does not fulfill this requirement is at best of limited and transitory value. A system must be so detailed that any researcher acquainted with the rules may be assured of locating the position of a desired compound even though that compound has not yet been placed in the system. Although all chemists will not agree on what constitutes an adequate description of a compound, most chemists would accept a unique name or a structural formula, together with some reproducible distinguishing physical property where stereoisomerism is possible.

Of secondary importance is the requirement that a system be logical. Unless the basis for the system is readily understood and unless the rules are easily remembered by those applying them, the system will never prove popular. Obviously, any system should utilize as far as possible the concepts commonly accepted by those who will be using the system. The basic rules should not be foreign to the thinking of chemists, and the general arrangement should follow approved patterns.

Third in order of importance is the requirement that the system group together compounds of similar and graded physical, chemical, and pharmacological properties. To the extent that a system achieves this goal, it will, of course, be logical. On the other hand, a system might conceivably be logical to the user and still make no attempt to correlate structure and properties.

A system which meets only the first requirement will enable a user to locate any desired compound; a system which also meets the second requirement will enable a user to locate the desired compound with facility; a system which meets all three requirements will make possible the rapid comparison of chemical structures exhibiting certain significant properties and will enable the user to draw generalizations for the direction of further research.

In our opinion all other requirements are subordinate to these three; however, a few other requirements deserve serious consideration. A system should be versatile, economical to set up, and economical to operate. Thus a system should be adaptable to a wide variety of index forms, yet should not demand equipment not ordinarily available. It should be possible to teach a person with a minimum of scientific training to use the system within a few hours. Once the position of a compound in the system has been determined, the filing of that compound, a clerical operation, should not require the services of an expert familiar with the principles of the system.

Before discussing the background of the Survey

[1] Presented before the Division of Chemical Education at the 109th meeting of the American Chemical Society in Atlantic City, April 8–12, 1946.

[2] The Survey of Antimalarial Drugs was established in the Division of Chemistry and Chemical Technology of the National Research Council under the supervision of the Divisional Chairman, W. Mansfield Clark. The work was carried out in the Department of Chemistry and in the School of Medicine of the Johns Hopkins University, Baltimore, Maryland, and terminated July 31, 1946.

[3] To be published by Edwards Brothers, Inc., Ann Arbor, Michigan.

system, we should like to consider the other systems in common use today and to note some of their respective advantages and disadvantages. In the more widely used systems, compounds are arranged by name (index to *Chemical Abstracts*[4]), by molecular formula (indexes to *Chemical Abstracts* and to *Chemisches Zentralblatt*), by physical properties (Huntress and Mulliken, "Identification of Pure Organic Compounds"[5]), and by structure (Beilstein, "Handbuch der Organischen Chemie").

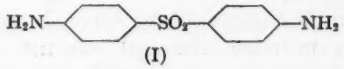
If a unique name could be assigned to each compound, the names could be arranged in alphabetical order and a compound could be located by the same procedure used to locate a word in a dictionary. An ideal system based on nomenclature might be expected to be logical and, to some extent, to group together compounds having similar properties; however, only one group, the editors of *Chemical Abstracts*, has made any concerted effort in this direction. Over a period of 30 years there has developed in the indexes of *Chemical Abstracts* a system for naming compounds. Interestingly enough, the objective of the editors was not to develop a system for the *classification* of compounds, but rather a system for the *indexing* of compounds. These two objectives are not necessarily identical. Indeed, the quality of the name indexes to *Chemical Abstracts* is so high and the cross references are so abundant that few people realize the magnitude of the difficulties inherent in a classification system based on nomenclature. In spite of these difficulties, however, a number of groups are now using the indexing system of *Chemical Abstracts* as a classification system.

In *Chemical Abstracts* a relatively small number of compounds are selected as stem compounds, and all others are treated as substituted derivatives of these parents. Each compound is indexed first under the parent and then according to the modifying radicals arranged in alphabetical order; however, in *Chemical Abstracts* the system is sacrificed for compounds bearing trivial names, which are used wherever possible.

The principal advantages of the *Chemical Abstracts* system are (1) the economy in labor, since it is necessary to name a compound for the purpose of talking about it, and (2) the economy in space, in which the system excels all other types of system. The principal disadvantages of the *Chemical Abstracts* system and, in fact, of any system based on nomenclature lie in (1) the complex nature of the rules governing the assignment of names and (2) the complexity of the names themselves, which often makes it necessary for a reader to write down a structure before he can grasp what is implied by the name.

In a compound having several functional groups and rings, it is often difficult, if not impossible, to determine what constitutes the main function and therefore under which stem compound the structure will be indexed. The use of trivial names nullifies any attempt to render a system logical or to group together compounds having similar physical properties. An apparent advantage in a system of nomenclature, the fact that names can be transcribed on a typewriter by anyone unfamiliar with their meaning, is to a considerable extent offset by the presence of Greek letters, italicized letters, and other characters (superscripts, subscripts, brackets, braces) rarely found on commercial machines.

Although the system of nomenclature developed by the editors of *Chemical Abstracts* does not constitute a satisfactory system of classification, this does not imply that we have any criticism of *Chemical Abstracts* names. On the contrary, we wish to commend the editors of *Chemical Abstracts* for their courage in bringing some order out of chaos and to support them wholeheartedly in encouraging all chemists to use *CA* names. It should be noted that the liberal use of cross references in *Chemical Abstracts*, made possible by the economy of space inherent in the nomenclature system, greatly facilitates the location of compounds by those not familiar with the rules. Thus, although it is often difficult to locate a compound in *Chemical Abstracts* by the approved name, it becomes a simple task with the aid of cross references to find the compound uniquely described by another name. A single example will illustrate this point. The compound represented by the structure I is popularly called *p,p'*-diaminodi-



(I)

phenylsulfone but is indexed in *Chemical Abstracts* as *aniline, p,p'*-sulfonyldi-, because an amine takes precedence over a sulfone as the principal function of a molecule; however, *Chemical Abstracts* adds the cross reference, *sulfone*, bis(*p*-aminophenyl)-, so that a person unfamiliar with the rules may readily locate the compound.

A second type of arrangement of compounds is by molecular formula. The number of atoms of each element in a compound is calculated and the symbols for the elements, followed in each case by a subscript designating the number of atoms of that element, are set down in some arbitrary order. Thus, in the *Chemical Abstracts* system the arrangement of the elements is in the alphabetical order of their symbols except for organic compounds, in which carbon and hydrogen are always placed at the beginning of the formula. The formulas are arranged alphabetically and according to the number of atoms of each element present. In this latter operation each element takes precedence over all others to the right of it in the formula. A variation of this system is used in *Chemisches Zentralblatt*, where the total number of different elements constitutes a special subdivision.

The accuracy in the calculation of a molecular formula makes for a simple and straightforward system which in one step breaks down all compounds into

[4] *Chemical Abstracts*, **39**, 5867–975 (1945).

[5] HUNTRESS, E. H., AND S. P. MULLIKEN, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1941.

groups of isomers. Unfortunately, since the molecular formula alone is inadequate to distinguish isomers, the formula must be supplemented by a name or structural formula. Moreover, it is necessary to superimpose an additional arrangement for isomers, an arrangement which is totally unrelated to the molecular formula.

The chief advantage of a molecular-formula index is its simplicity, and the system is useful where such a small number of compounds are involved that a compound may be picked out of its isomers by inspection; however, the system does not, except in a narrow sense, relate structure to physical, chemical, or pharmacological properties. Polymers, quaternary ions, and salts, which require special rules in any classification system, are particularly troublesome in a system based on molecular formula. Finally, the operation of the system is a laborious and slow process since the molecular formula must be calculated each time the location of a compound is sought.

It is apparent that in any organization of compounds chemists think in terms of structure. Structure to the chemist means ions and molecules, rings and chains, functional groups and nonfunctional skeletal material. He indicates the structure of a compound by the highly conventionalized structural formula. There is little doubt that a well-written structural formula can be read more rapidly than any other means for conveying the same information. Therefore, the most appealing type of classification system to the chemist must be based on the structural formula. Moreover, the general structural pattern has already been established since the popular comprehensive treatises and textbooks are remarkably similar in the order of treatment of subject matter. The design of an intelligent classification system, accordingly, involves merely setting down the rules to locate uniquely those compounds for which several relative positions would at first sight appear equally probable. The gross pattern has already been established by custom.

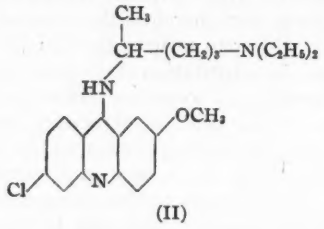
Although many groups have undertaken the classification of a limited number of compounds by structure, we are acquainted with only one comprehensive, all-inclusive system. This system, developed by the editors of Beilstein's "Handbuch der Organischen Chemie," fully meets the primary requirement in uniquely locating every compound for which a structure is known. Moreover, the editors have made an obvious attempt to follow the concepts of chemists at the time, as well as to group together compounds having similar properties. The Beilstein system is so unnecessarily complex, however, and so illogical to modern chemists that it is used with considerable reluctance even by those who appreciate the information available in the "Handbuch."

In the Beilstein system all compounds are first divided into two groups, depending upon the presence or absence of a cyclic system. The cyclic compounds are then subdivided into several groups depending upon the nature of and the number of elements present in the rings. No attention is paid at this stage to the type or size of the ring and, indeed, this is of interest only at the ultimate stage of classification. Having defined the main division into which a compound falls, Beilstein treats all compounds therein as derived from certain parents characterized by particular functional groups. In order to reduce the total number of functional groups and therefore the number of classes in the system, Beilstein utilizes the formal operations (1) hydrolysis, (2) substitution of nonfunctional groups, and (3) replacement, in some cases, of sulfur, selenium, or tellurium, by oxygen. A structure must be examined, in turn, for each operation and, if applicable, each operation leads to a new and simpler parent compound. The ultimate parent compounds are then arranged within the class according to the degree of unsaturation, as determined by calculating the value of x in the expression C_nH_{2n-x}, where n is the number of carbon atoms in the formula and $(2n - x)$ is the number of hydrogen atoms present. Compounds within a class having a common value for x are said to be in a given rubric. They are arranged within the rubric according to molecular formula.

The treatment of compounds as derivatives of others in a stepwise sequence of operations is the most serious defect in the Beilstein system, for it requires the user to consider several specific structures in addition to the one with which he is directly concerned. He must first determine the structures of each parent compound, in order, and then locate each, in reverse order, before he can finally locate the compound originally sought.

The capriciousness of the operations in Beilstein, the illogical distinctions between rings and acyclic compounds, and the unnecessary introduction of the degree of unsaturation as a subdividing group constitute additional and strong arguments against the Beilstein system. Thus, for example, such dissimilar rings as ethylenimine, pyrrole, and pyridine are grouped together simply because they are heterocyclic compounds and each contains one atom of nitrogen in the ring. Acetic anhydride is hydrolyzed to, and therefore considered a derivative of, acetic acid, which falls early in the system as an acyclic compound. Succinic anhydride, a similar compound, falls late in the system because it is cyclic and is considered as a diketone. A mercaptan is regarded as a "replacement" derivative of the corresponding alcohol, whereas a sulfonic acid is recognized as a functional group in its own right. Secondary and tertiary amines must be hydrolyzed since only a primary amine is recognized as a functional group; often the hydrolysis products are different depending upon which C—N bond is broken, and a decision must be made for each compound on how to conduct the hydrolysis. The treatment of polyfunctional compounds is inconsistent; thus, compounds containing one "oxy" group precede compounds containing one "oxo" group. On the other hand, compounds containing one each of an "oxy" group and an "oxo" group follow compounds containing two or more "oxy" or two or more "oxo" groups.

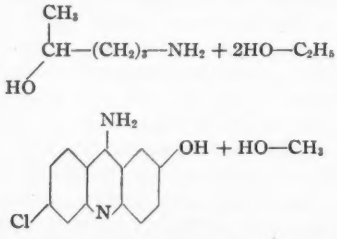
The complexities of the Beilstein system are illustrated by recording the operations required to locate a compound. A suitable, representative example is quinacrine, 6-chloro-9-(4-diethylamino-1-methylbutylamino)-2-methoxyacridine (II). The structure bears a



(II)

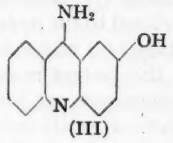
methoxy group and a chlorine atom bound to an acridine ring. Attached to the ring is a nitrogen atom in the form of a secondary amine, and the structure contains a tertiary aliphatic-amino group.

In the Beilstein system the structure must first be examined for the possibility of hydrolysis. Since Beilstein does not recognize ethers or secondary or tertiary amines as functional groups, a series of hydrolysis operations must be carried out. The hydrolysis of an ether is straightforward, but the hydrolysis of an unsymmetrical amine may give different products depending upon which C—N bond is broken. Accordingly, it is necessary to carry out all possible hydrolyses in order to decide which route should be followed. Thus, the hydrolysis of quinacrine by one route yields methyl alcohol, ethyl alcohol, 1,4-pentanediamine, and 6-chloro-2,9-acridinediol; by a second route the products are methyl alcohol, ethylamine, ethyl alcohol, 1,4-pentanediol, and 9-amino-6-chloro-2-acridol; by the third route the products are methyl alcohol, ethyl alcohol, 5-amino-2-pentanol, and 9-amino-6-chloro-2-acridol. Because in the system 9-amino-6-chloro-2-acridol follows all other possible hydrolysis products and because 5-amino-2-pentanol follows ethylamine or 1,4-pentanediol, the third route is the required one.[6]



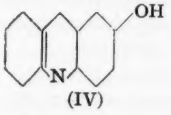
FORMAL HYDROLYSIS PRODUCTS OF QUINACRINE IN THE BEILSTEIN SYSTEM

The hydrolysis operation yields a parent compound which in turn must be examined for the presence of any nonfunctional groups. The parent compound, 9-amino-6-chloro-2-acridol, contains chlorine which must be substituted by hydrogen. The new parent compound so obtained, 9-amino-2-acridol (III), contains no



(III)

sulfur and so no replacement operation is involved. These operations have yielded a structure for which there is a definite location in the system, and the next step is the location of the parent compound. 9-Amino-2-acridol falls in the heterocyclic division among the compounds containing one atom of nitrogen in the ring. It possesses two functional groups, an amine and an alcohol, and is filed with the amines but is identified as an amino derivative of the ultimate parent, 2-acridol (IV). It is now necessary to calculate the



(IV)

molecular formula of 2-acridol in order to calculate the value of x in the expression, C_nH_{2n-x}. The value of x so calculated is 17, and 2-acridol will be filed with all analogs having the same degree of unsaturation. Ultimately the 2-acridol is located within the rubric by its molecular formula, $C_{13}H_9ON$. Having located the 9-amino derivative of 2-acridol, the essential processes must be reversed and the replacement, substitution, and hydrolysis products considered in order to locate, at last, the quinacrine originally sought. It is not surprising that the average graduate student takes ten minutes to locate a compound in Beilstein.

The basis of the Survey classification system is a fundamental unit of structure designated as the *functional unit*. Under this heading are included (1) *functional groups* and (2) ring systems which are defined, for the purposes of classification, as *functional rings*. The justification for including functional rings along with functional groups is the fact that functional rings contribute to the physical, chemical, and pharmacological properties of compounds in the same sense as do functional groups; moreover, this method of definition groups together compounds containing the same ring systems.

The Survey system organizes compounds solely on the basis of the nature and arrangement of the functional units of which each compound is composed. To achieve this end, the functional units of a compound are considered in decreasing order of importance, and the order of importance is rigidly fixed by the order of appearance of the functional units in the system. The fundamental rule which controls the position of compounds is identical with a principle of the Beilstein

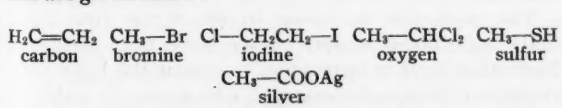
[6] In actual practice, the rules governing hydrolysis are not as simple as is implied here. For example, N-phenyl-*p*-phenylenediamine is treated as a coupling product of *p*-phenylenediamine and phenol rather than as a coupling product of *p*-aminophenol and aniline despite the fact that *p*-aminophenol follows *p*-phenylenediamine in the system.

system—namely, when a compound contains two or more functional units, the functional units are invariably taken in that order which will place the compound at the latest possible position in the system. Therefore, in filing a compound, one must consider (1) that functional unit (designated as the *principal functional unit*) appearing last in the system, (2) that functional group appearing next to last, and so on. For example, 2-hydroxyethanesulfonic acid contains two functional units—(1) an aliphatic sulfonic acid and (2) an aliphatic alcohol. Since an aliphatic sulfonic acid comes later in the system than an aliphatic alcohol, this compound will be located primarily with the aliphatic sulfonic acids, and, more specifically, with the aliphatic-sulfonic-acid compounds which contain an aliphatic alcohol.

The order of appearance of functional units is logical and easily remembered. The position in the system of a functional unit of a compound depends primarily on the elements of which it is composed, secondarily on the manner of attachment of the unit to the remainder of the molecule, and finally, on the chemical nature of the functional unit itself. The manner in which the position of functional units is determined is set forth in the following paragraphs.

The primary divisions of the Survey system correspond to the chemical elements, and the division of an individual functional unit is determined by that element contained therein which falls last in the system. All other elements of the functional unit are ignored in so far as the division is concerned. The more common elements fall in the order hydrogen, carbon, fluorine, chlorine, bromine, iodine, oxygen, sulfur, nitrogen; the remaining elements follow nitrogen in order of increasing atomic number. An element takes precedence over all elements which precede it and is subordinate to all elements following it.

Since the gross position of a compound in the system is fixed by the functional unit appearing last in the system and since the gross position of a functional group depends in the first case upon its elements, it follows that all compounds are arranged primarily according to the elements they contain. For convenience, the *principal division* of a compound is defined as the division of its principal functional unit. With the exception of a very small number of compounds,[7] compounds may be sorted into the ninety-six or more possible principal divisions based solely on the elements present in the molecular formula; no reference to the structure is needed. Some representative compounds and the divisions into which they fall are given below:

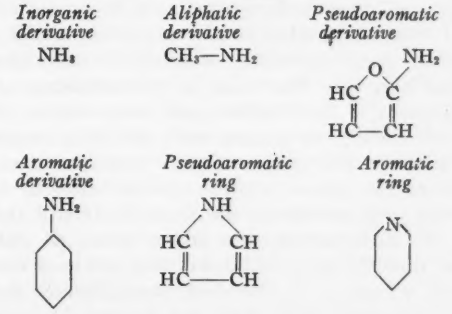


[7] Compounds containing two or more halogen atoms on the same carbon atom are formally hydrolyzed to aldehydes, ketones, or acids, as the case may be, and therefore fall in the oxygen division even though they contain no oxygen.

The separation of compounds into 96 or more principal divisions, depending upon the elements present in the functional units, was selected as the primary classification step because of its extreme simplicity and because of the desire to obtain as many categories as possible without taxing logic or memory. By placing carbon and hydrogen as the least important elements, the organic hydrocarbons are made to appear first, and the system thereby parallels almost every comprehensive treatise and textbook. Similarly, the treatment of fluorine, chlorine, bromine, iodine, oxygen, sulfur, and nitrogen in order follows a generally approved pattern. The remaining elements are placed in order of increasing atomic number primarily because of the simplicity of this arrangement. A significant consequence of this scheme is to group together organic compounds containing a heavy metal. This is a logical procedure since interest generally centers around the foreign element in an organic compound. Because this arrangement separates different metal salts of the same acid and places each in the respective metal division, lithium, sodium, potassium, magnesium, and calcium were made exceptions. All compounds of these elements are considered to be salts and are filed immediately after the corresponding acids.

The functional units characterized by a common element, and therefore falling within a single division, are separated into six classes, depending upon the structural characteristics of the functional units. The classes are, in order of appearance, (1) inorganic derivatives, (2) aliphatic derivatives, (3) pseudoaromatic derivatives, (4) aromatic derivatives, (5) pseudoaromatic rings, and (6) aromatic rings. In the first four classes the functional unit is a functional group, and the class designates the nature of the nucleus to which the group is attached. In the last two classes the functional unit is a functional ring, and the class designates the size and bond structure of the ring. The following compounds illustrate the six classes in the nitrogen division:

REPRESENTATIVE EXAMPLES OF THE SIX CLASSES IN THE NITROGEN DIVISION



The selection of the six classes as a secondary stage in the classification of compounds was adopted because of our desire to recognize the profound effect of the nucleus on the properties of a functional group. Thus the compounds cyclohexylamine, aniline, pyrrole, and

pyridine could conceivably be regarded as amines; yet the physical and chemical properties are so widely different that such a classification could hardly be of general use. On the other hand, piperidine, a heterocyclic compound, resembles closely the simple, secondary aliphatic amines.

Chemists have long regarded such heterocyclic rings as furan, thiophene, and pyrrole as belonging in a special class, a class characterized by unusual stability—at least in comparison with their acyclic analogs—and by properties resembling those of benzene, pyridine, and other so-called aromatic compounds. The inherent stability of these two types of ring system has been rationalized recently by the resonance or electromerism concepts, and today chemists are generally agreed that unusual stability is associated with a structure for which two or more electromeric forms can be drawn. We have incorporated this concept in the Survey system by recognizing two, and only two, types of functional rings. A pseudoaromatic ring has a bond structure similar to pyrrole, thiophene, or furan, regardless of the atoms present in the ring. An aromatic ring has a bond structure similar to that of benzene, pyridine, or the pyrylium ion, regardless of the atoms present in the ring. All other rings are considered to be nonfunctional and, as rings, play no role in fixing the position of a structure in the system.

A fused-ring system is recognized as functional provided that each ring making up the system is also functional. Thus benzene, naphthalene, and phenanthrene are recognized as distinct aromatic-ring systems. 1,2,-3,4-Tetrahydrophenanthrene, however, is regarded as a dialkyl derivative of naphthalene, and 9,10-dihydrophenanthrene is regarded as two benzene rings.

The classes in which the element is part of a functional ring are placed last in order to group together, as far as possible, all compounds containing a given functional ring system. Thus all compounds containing the quinoline ring fall together unless, of course, a more important functional unit is also present.

If the functional unit is a functional group, the class designates the nucleus to which the group is attached. A functional group is designated as an inorganic derivative if it is not attached to carbon; otherwise, it is an aliphatic, pseudoaromatic, or aromatic derivative as the case may be. For example, a consequence of this arrangement is that aniline and benzylamine fall in different classes, an arrangement which is consistent with the great differences in their dissociation constants. In aniline the amino group is attached directly to an aromatic ring, and hence the class is aromatic derivative. In benzylamine the amino group is not attached directly to a functional ring but is separated from it by carbon; it, therefore, is an aliphatic derivative.

Just as a functional unit is associated with but one division, it is also associated with but a single class. If a polycovalent functional group, such as an ether, is attached to different types of nuclei, the class is always selected so as to place the functional unit as far back as possible in the system. Thus anisole (methyl phenyl ether) is treated as an aromatic, rather than an aliphatic, ether.

The third classification stage groups together identical functional units falling within identical classes and identical divisions. The more important functional units are listed in the accompanying outline of the Survey system. Functional rings comprise all simple pseudoaromatic and aromatic rings and all fused-ring systems in which each ring is functional. The order of appearance of different ring systems falling within the same class is one of increasing complexity. Functional groups comprise all different combinations of atoms excluding (1) functional rings, (2) carbon-carbon bonds, and (3) those combinations subject to certain operations detailed below. The order of appearance of functional groups follows the same general pattern for all elements. Bonds of one element to other elements are treated in order of the appearance of the elements in the Survey system; nonhydrolyzable bonds between any two given atoms are treated in the order single, double, triple.

When the principles on which the Survey system is based are understood, the location of a compound is simple, sure, rapid, and logical. For example, again consider the structure of quinacrine (II) which is so troublesome to locate in the Beilstein system. The structure is first examined for the application of any operations necessary to yield functional units, operations which are discussed below; however, in this case as in most cases, no operations are required. The second step is to set down, mentally or on paper, the functional units, together with their respective divisions and classes, in the order of their importance, *i. e.*, the inverse order of their appearance in the system. They follow:

	Principal functional unit	*Second functional unit*	*Third functional unit*	*Fourth functional unit*	*Fifth functional unit*
Division	Nitrogen	Nitrogen	Nitrogen	Oxygen	Chlorine
Class	Aromatic ring	Aromatic derivative	Aliphatic derivative	Aromatic derivative	Aromatic derivative
Functional unit	Acridine	Amine	Amine	Ether	Chlorine

Quinacrine is located in that section characterized by the combination of functional units listed above. It follows all compounds in that section containing a smaller number of carbon atoms and precedes all compounds containing a larger number of carbon atoms. In the same section will be found all homologs involving variations in the side chain as well as compounds in which the substituents are in other positions on the acridine ring.

The principles according to which the functional units are ranked in importance have been outlined. Nevertheless, it is instructive to review the logic with regard to the specific example, quinacrine, in order to make the full meaning of the above table quite clear. Quinacrine contains five functional units, each characterized by one element other than carbon: (1) acridine ring, (2) aromatic amine, (3) aliphatic amine, (4)

aromatic ether, (5) aromatic chlorine. Since the first division of functional units is by elements, we search for those functional groups which contain that element which falls last in the Survey system. The only elements in quinacrine are C, H, Cl, N, and O. N falls last in the system, and therefore the principal functional group must be (1) acridine ring, (2) aromatic amine, or (3) aliphatic amine. In order to ascertain which of the three nitrogen-containing functional units is most important, it is necessary to observe that (1) is classed as an aromatic ring, (2) as an aromatic derivative, and (3) as an aliphatic derivative. It will be recalled from the discussion of class that in the system derivatives fall in the order aliphatic derivative, aromatic derivative, aromatic ring. Therefore, the acridine ring is the functional unit which falls last in the system and is, accordingly, the principal functional unit.

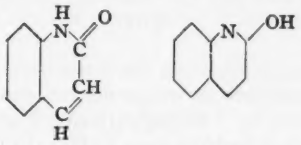
In a like manner it can be shown that the aromatic amine ranks second in importance, and the aliphatic amine third. The aromatic ether and aromatic chlorine fall in the divisions oxygen and chlorine, respectively, which accounts for their relegation to fourth and fifth places.

Since the principal functional unit determines the gross location of a compound, quinacrine will be found in the principal division *nitrogen* and the principal class *aromatic ring*, grouped with all other compounds containing acridine rings and no other functional units of greater importance. Furthermore, quinacrine will be grouped with those compounds containing an acridine ring and an aromatic-amino group—more specifically, with those containing, in addition, an aliphatic-amino group, and so on.

There must inevitably arise, in any classification system, certain cases where the general pattern fails to apply or, if applied literally, leads to a relatively poor arrangement. (1) If in the Survey system every new combination of atoms were treated as a new functional unit, sooner or later the total number of different functional units would grow so large as to be unmanageable. (2) Many compounds are represented by two different, tautomeric structures; such compounds should be filed in one place if this is possible. For these reasons the Survey system utilizes three formal operations, and each structure must be examined for their possible application before the functional units may be listed. These operations are designed to convert nonfunctional units into functional units or, alternatively, to convert functional units into others which would fall later in the system. The operations involve (1) a shift of electrons or bonds in the structure, (2) a shift of hydrogen atoms and bonds in the structure, and (3) hydrolysis. These are formal operations in that they follow certain prescribed rules; they are most conveniently explained by specific examples.

Compounds which are hydrolyzable in the laboratory are generally associated closely with their hydrolysis products. Thus, urea is closely associated with ammonia and carbonic acid, acetyl chloride with acetic acid and hydrochloric acid, ethyl acetate with acetic acid and ethyl alcohol. Therefore, in the Survey system acetals, esters, acid halides, acid anhydrides, amides, oximes, nitriles, and similar compounds are not recognized as functional units but are formally hydrolyzed and considered to possess the functional units of the carboxylic-acid hydrolysis products. Thus, acetic anhydride is considered to possess two carboxylic-acid groups and is filed along with succinic acid. Methyl formate is considered to possess an aliphatic carboxylic acid and an aliphatic alcohol and will be filed with glycolic acid.

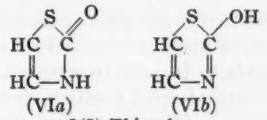
A second type of classification problem is exemplified by carbostyryl for which two tautomeric forms are commonly written. Form V*a* appears to be an amide and would normally be classified as (1) an aromatic amine, (2) an aliphatic carboxylic acid, and (3) a benzene ring. Form V*b* would be classified as (1) a quinoline ring and (2) an aromatic alcohol.



(V*a*) (V*b*)

Carbostyril

Since form V*b* would follow form V*a* in the Survey system, form V*b* is preferred. Accordingly, if by tautomerism a ring may be converted to a functional ring, the structure is classified as though it were in the tautomeric form. In such a case the tautomerism operation takes precedence over any possible hydrolysis operation. The tautomerism of 2(3)-thiazolone (VI) illustrates the formation of a pseudoaromatic ring.



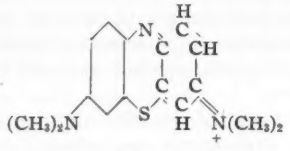
(VI*a*) (VI*b*)

2(3)-Thiazolone

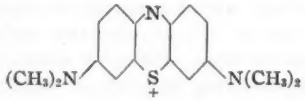
The tautomerism operation is also utilized in certain specific instances for the purpose of bringing together two mobile tautomers of different structure. Thus, for example, the aliphatic combination C=C—OH is not recognized as such; all compounds having this structure are classified as though in the tautomeric carbonyl form. By this arrangement both the keto and enol forms of ethyl acetoacetate are filed together in the section characterized by (1) an aliphatic carboxylic acid, (2) an aliphatic ketone, (3) an aliphatic alcohol. In all cases the tautomerism operation is restricted to the moving of a hydrogen atom to a relatively negative atom.

The third type of operation, electromerism, is used solely for the purpose of creating functional rings and, where applicable, takes precedence over hydrolysis. Electromerism involves essentially the shift of one or more electron pairs, giving an excited state with charge separation but resulting in a structure which meets the

requirements of a functional ring. The advantages of this type of operation over the only alternative, hydrolysis, are best illustrated in the dye, methylene blue, for which the two significant electromeric forms are given below. Form VII*b* has the advantage over form VII*a* in yielding a single, symmetrical aromatic-ring system for which no hydrolysis is necessary.

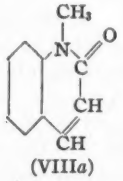


(VII*a*)

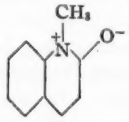


(VII*b*)

An example illustrating the conversion to an excited state of a structure in whose normal state there is no charge is given by 1-methylcarbostyril which is classified as though it had the form VIII*b*. In this form it is (1) a quinolinium ion and (2) an aromatic alcohol.



(VIII*a*)

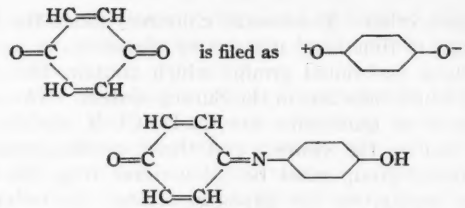


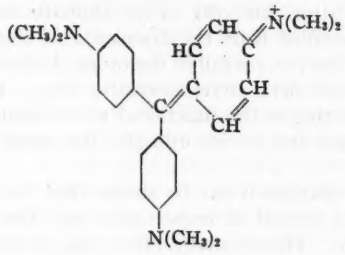
(VIII*b*)

It will be noted that in the above examples all charged atoms retain their normal octets of electrons. In a few cases it is desirable to be able to write excited states in which one atom has a formal positive charge and only a sextet of electrons. This particular type of electromerism is restricted to the formation of aromatic rings and is used only for quinones, their thio analogs, quinonimines, and dyes of the triphenylmethane type. The operation is best described in terms of three representative examples in the next column.

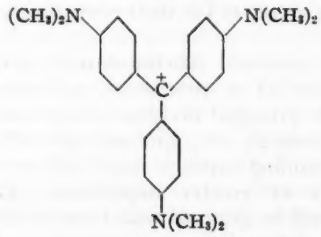
Rules governing the electromerism, tautomerism, and hydrolysis operations are detailed below.

In the use of a system of classification based on structure, especially if a rapid comparison is to be made between different structures in which there are only minor variations, it is desirable to draw the structures according to a rigidly set pattern. Therefore, the drawing of structures becomes an essential part of the classification system. In our work, all functional rings are oriented in accordance with the "Ring Index;"[8] where two rings are present, precedence is assigned to that ring which appears last in the Survey system. In a

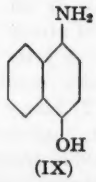




is filed as



symmetrically substituted ring the orientation is designed to give the most important functional group the lowest possible number on the ring, even though it is not consistent with the approved *Chemical Abstracts* name. For example, 4-amino-1-naphthol is oriented as



(IX)

in (IX) because the amino group takes precedence over the hydroxyl group. Structural formulas are drawn with care and, as nearly as possible, to scale. Aromatic rings are represented by plain hexagons; no attempt is made to indicate the presence of the double bonds. On the other hand, for all other rings the atoms and bonds are represented. The use of stencils prepared according to the dimensions given in the figures makes possible the typing of both horizontal and vertical rings provided that elite type is used (12 characters to the inch, six lines to the inch).

Tables 1 to 9 show the order of appearance of structures in various divisions of the Survey system. These tables were selected from "A Survey of Antimalarial Drugs, 1941–1945."[8]

[8] PATTERSON, A. M., AND L. T. CAPELL, "The Ring Index," Reinhold Publishing Corporation, New York, 1940.

Experience in the filing of nearly 15,000 different structures has convinced us of the superiority of the Survey system over all others known to us. An average time of only eight hours is required to train a person who has had one year of organic chemistry. One can expect a conscientious worker with no more training to file 90 per cent of all structures without hesitation.

SURVEY CLASSIFICATION SYSTEM

Rules and Definitions

I. The *Functional Unit* is a structural combination of atoms which forms the basis for the relative location of compounds in the Survey system. Functional units comprise both functional rings and functional groups.

Functional Rings include all pseudoaromatic rings and all aromatic rings and all combinations of such rings having one or more sides in common.

Functional Groups include all other combinations of atoms except (*a*) those containing exclusively carbon and hydrogen and (*b*) those to which the operations described in paragraphs IV, V, VI, and VII apply.

An *Aromatic Ring* is any six-membered ring containing alternate double and single bonds.

A *Pseudoaromatic Ring* is any five-membered ring containing three single and two conjugated double bonds in which the atom held in the ring by two single bonds has a free pair of electrons not shared with another atom.

The relative order of appearance of the more common functional units is given below.

II. The *Class* comprises a group of functional units characterized by having in common either (1) a given type of functional ring or (2) a given type of nucleus to which the functional groups are attached. The six recognized classes are, in order of appearance: (1) inorganic derivatives, (2) aliphatic derivatives, (3) pseudoaromatic derivatives, (4) aromatic derivatives, (5) pseudoaromatic rings, (6) aromatic rings.

Class 6, aromatic rings, includes all functional units in which the important element is in an aromatic ring.

Class 5, pseudoaromatic rings, includes all functional units, except those in class 6, in which the most important element is in a pseudoaromatic ring.

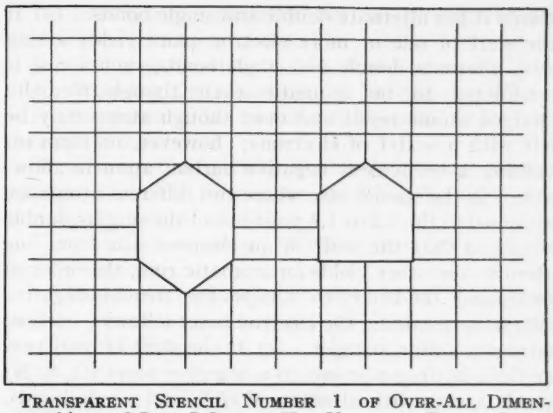
Class 4, aromatic derivatives, includes all functional units, except those in classes 5 and 6, in which the most important element is in a functional group attached directly to an aromatic ring.

Class 3, pseudoaromatic derivatives, includes all functional units, except those in classes 4 to 6, in which the most important element is in a functional group attached directly to a pseudoarmatic ring.

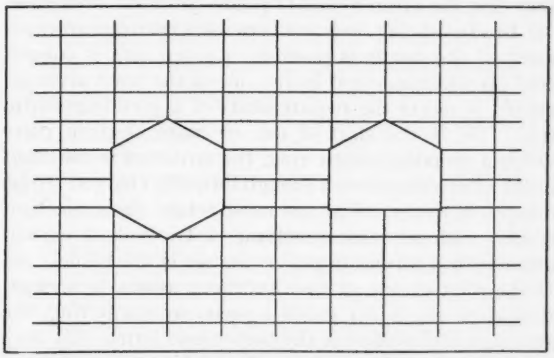
Class 2, aliphatic derivatives, includes all functional units, except those in classes 3 to 6, in which the most important element is in a group attached to carbon.

Class 1, inorganic derivatives, includes all functional units in which the most important element is in a functional group not attached to carbon.

III. The *Division* comprises all functional units having a common element provided that the element is the most important in the unit. The order of increasing importance of the elements is defined as follows: hydrogen, carbon, fluorine, chlorine, bromine, iodine, oxygen, sulfur, nitrogen; the remaining elements follow nitrogen in order of increasing atomic number. Compounds of lithium, sodium, potassium, magnesium, and calcium are exceptions, and compounds containing these elements are treated as salts and filed under the corresponding parent acids.



TRANSPARENT STENCIL NUMBER 1 OF OVER-ALL DIMENSIONS $^1/_{16} \times 3.5 \times 5$ INCHES HAS VERTICAL, ETCHED LINES SPACED FOUR TO THE INCH AND HORIZONTAL, ETCHED LINES SPACED SIX TO THE INCH. THE PENTAGONAL AND HEXAGONAL RINGS ARE CUT OUT SO THAT EACH SIDE IS $^1/_{80}$ INCH OUTSIDE OF THE ETCHED LINES. IN THIS WAY A WRICO RULING PEN WITH A NUMBER SEVEN POINT (RADIUS, $^1/_{80}$ INCH) GIVES RINGS CORRESPONDING PRECISELY TO THE SPACINGS OF ELITE TYPE, 12 CHARACTERS TO THE INCH, SIX LINES TO THE INCH. IN ADDITION TO ITS USE FOR DRAWING VERTICAL RINGS, THIS STENCIL MAY BE USED FOR HORIZONTAL HEXAGONAL RINGS IF THE TYPEWRITERS BEAR A HALF-SPACE GEAR, WHICH MAKES POSSIBLE 12 LINES TO THE INCH.



TRANSPARENT STENCIL NUMBER 2 DIFFERS ONLY IN THAT THE VERTICAL LINES ARE SPACED THREE TO THE INCH. IT IS PARTICULARLY USEFUL FOR ALICYCLIC RINGS AND CAGES SUCH AS QUINUCLIDINE.

IV. *Aromatization* is a formal process by which slight alterations in the structure normally assigned to certain six-membered rings make them aromatic. In such cases the rings are classified as though they had the altered, aromatic structure. (*a*) In a fused-ring system where more than one arrangement of the bonds is possible, a given ring is considered to be aromatic if in any one of the possible bond arrange-

ments it has alternate double and single bonds. (*b*) If the shift of one or more electron pairs yields a ring with alternate double and single bonds, such a ring is considered to be aromatic even though formally charged atoms result and even though atoms may be left with a sextet of electrons; however, no form involving a tricovalent negative carbon atom is allowable. In the special case where two different atoms are attached to the 1,2 or 1,4 positions of the ring by double bonds so that the shift of an electron pair from one atom to the other yields an aromatic ring, the order of increasing tendency to accept the formal negative charge by retaining the electron octet follows: carbon, nitrogen, sulfur, oxygen. (*c*) If the shift of one, two, or three hydrogen atoms to a negative atom (O, S, N) yields a ring with alternate double and single bonds, such a ring is considered to be aromatic. (*d*) Any combination of operations (*b*) and (*c*) is allowable; however, tautomerism among groups attached to a potential fused-aromatic-ring system is allowable only if all groups are attached to the same ring.

V. *Pseudoaromatization* is a formal process by which slight alterations in the structures assigned to certain five-membered rings make them pseudoaromatic. In such cases the rings are classified as though they had the altered (see I) pseudoaromatic structure. (*a*) In a fused-ring system where more than one arrangement of the bonds is possible, a given ring is considered pseudoaromatic if in any one of the bond arrangements, it meets the requirements of a pseudoaromatic ring. (*b*) If the shift of one or more electron pairs yields a pseudoaromatic ring, the structure is classified in the altered form even though formally charged atoms result; however, all atoms must retain their electron octets, and no form involving a tricovalent carbon atom with a formal negative change is allowable. (*c*) If the shift of one or two hydrogen atoms to a negative atom (O, S, N) yields a pseudoaromatic ring, the structure is classified as the tautomeric form. (*d*) Any combination of (*b*) and (*c*) is allowable.

VI. *Tautomerism* is a formal process involving the shift of one or more hydrogen atoms accompanied by the attendant rearrangement of bonds. It is designed (1) to convert certain functional groups to functional rings (paragraphs IV and V) and (2) to classify together certain compounds in which two structures are in mobile equilibrium. The following functional units, if not parts of an aromatic or pseudoaromatic ring system, are classified in the tautomeric forms:

$R_2C{=}CR{-}OH$	$= R_2CH{-}CO{-}R$	
$R_2C{=}CR{-}SH$	$= R_2CH{-}CS{-}R$	
	$= R_2CH{-}CO{-}R$	$+ H_2S$
$R_2C{=}CR{-}NHR$	$= R_2CH{-}CR{=}NR$	
	$= R_2CH{-}CO{-}R$	$+ RNH_2$
$R_2CH{-}NO$	$= R_2C{=}NOH$	
	$= R_2CO$	$+ H_2NOH$
$R_2CH{-}N{=}N{-}R$	$= R_2C{=}N{-}NHR$	
	$= R_2CO$	$+ H_2N{-}NHR$
$R_2C{=}NO_2H$	$= R_2CH{-}NO_2$	
$R(HO)C{=}CR(SH)$	$= RCO{-}CHR(SH)$	
$R(HO)C{=}CR(NHR)$	$= RCO{-}CHR{-}NHR$	
$RPH(O_2H)$	$= RP(OH)_2$	
	$= RP{=}O$	$+ H_2O$

VII. *Hydrolysis* is a formal process by which certain bonds are broken, and hydrogen and hydroxyl groups are added to the negative and positive fragments, respectively. The hydrolysis operation is carried out (*a*) whenever a negative group is attached to an atom by a multiple bond, and (*b*) whenever two or more negative groups are attached to a single atom. The hydrolysis operation is never carried out if it would break up a potential functional ring.

VIII. The *Section* comprises all compounds containing the same number of identical functional units in identical classes and divisions. Within a section compounds are arranged (1) in order of increasing number of carbon atoms, (2) in order of increasing number of hydrogen atoms, and (3) according to the following rules:

Arrangement of Isomers Within a Section[9]

Where possible the rules determining the relative positions of functional groups are extended to cover isomers. If necessary, nonfunctional groups, *e. g.*, C=C, are treated as functional. In cases where hydrolysis is carried out, the rules of the system or, when necessary, the special rules listed below are applied to that product which contains the principal functional unit. Where identical hydrolysis products are obtained, that isomer bearing the more heavily substituted principal functional group is placed last.

The following rules are applied, in the order of appearance. That isomer is placed last which has:

1. The greatest number of (*a*) aryl and (*b*) alkyl groups attached to functional rings in order of importance.
2. The functional rings in order of importance bearing the greatest number of groups in order of their importance.
3. The principal functional group attached (*a*) directly or (*b*) indirectly to the highest numbered position of the principal functional ring. Note that if the principal functional group is attached directly, any subordinate groups attached to the principal functional group are disregarded at this step.
4. The largest number of (*a*) triple bonds and (*b*) double bonds.
5. The largest number of carbon atoms attached (*a*) to aromatic nitrogen, (*b*) to pseudoaromatic nitrogen, (*c*) to aliphatic nitrogen.
6. The longest chain joining two principal functional units.
7. The most important functional unit attached to the longest chain joining two principal functional units.
8. (*a*) The longest chain attached to a chain joining two principal functional units, (*b*) this chain attached to the highest-numbered position of the chain joining two principal functional units.
9. (*a*) The largest number of carbon atoms attached to a chain joining two principal functional units;

[9] These rules, which are rather forbidding because of their necessarily detailed character, may be disregarded except where an unusually large number of isomers are involved. The rules are set down here only for completeness.

the highest-numbered position of attachment of a carbon atom on a chain joining the two principal functional units.

10. The longest end-chain attached (*a*) to a principal functional ring, (*b*) to a principal functional group.

11. The highest-numbered position of attachment of the longest end-chain on the principal functional ring.

12. (*a*) The longest chain attached to the longest end-chain attached to a principal functional unit, (*b*) this chain attached to the highest-numbered position of the longest end-chain.

13. (*a*) The largest number of carbon atoms attached to the longest end-chain attached to a principal functional unit, (*b*) the highest-numbered position of attachment of a carbon atom on the longest end-chain.

14. The second longest end-chain attached to a principal functional unit.

15. (*a*) The longest chain attached to the second longest end-chain attached to a principal functional unit, (*b*) this chain attached to the highest numbered position of the second longest end-chain.

16. (*a*) The largest number of carbon atoms attached to the second longest end-chain attached to a principal functional unit, (*b*) the highest numbered position of attachment of a carbon atom on the second longest end-chain.

Arrangement of Salts and Isomeric Rings

IX. For heterocyclic-ring systems isomers are arranged so that the hetero atoms in the ring have the lowest possible numbers, provided, however, that a new type of bond is not formed. For example, the order of the diazines is pyrimidine (1,3), pyrazine (1,4), and pyridazine (1,2), which contains an N—N bond.

For fused-ring systems the isomers are arranged (1) so that the most important single ring has the least number of rings fused to it and (2) so that the side of fusion will have the lowest possible numbers on the individual ring systems, in order of their importance. For example, (1) acridine is filed later than benzo[*f*] quinoline because two faces of pyridine are fused in the former, and only one face in the latter; (2) 1,8-naphthyridine precedes 1,5-naphthyridine because the former is a pyrid[2,3-*b*]pyridine whereas the latter is a pyrid[3,2-*b*]pyridine.

Salts are filed under the component which would be placed last in the system; however, sulfuric acid and phosphoric acid are exceptions, and salts of these acids are filed under the corresponding bases.

In groups attached to a pseudoaromatic ring if a nonhydrolyzable functional group is attached directly to the hetero atom, the derivative is placed at the end of the sections containing that ring.

Location of a Structure in the Survey System

X. Placing a single compound in the Survey system involves the following steps, in sequence.

1. Examine the structure for the presence of potential aromatic rings (IV).

2. Examine the structure for the presence of potential pseudoaromatic rings (V).

3. Examine the structure for tautomerism (VI).

4. Examine the structure for hydrolysis (VII).

5. Set down all functional units together with their corresponding classes.

6. Arrange the functional units in the order of their appearance in the Survey system with the aid of the accompanying outline.

7. Locate that section of the system in which the structure falls.

8. File the structure in its place in the section by use of the molecular formula and the rules for the location of isomers.

OUTLINE OF THE MORE IMPORTANT FUNCTIONAL UNITS IN THE SURVEY SYSTEM[10]

Division
  Class
    Functional Unit

Hydrogen
Carbon
  Aliphatic derivatives
    Tetracovalent carbon compounds and tricovalent anions
    Tricovalent carbon cations
  Pseudoaromatic derivatives
  Aromatic derivatives
  Pseudoaromatic rings
  Aromatic rings
    Benzene, Naphthalene, Phenanthrene, Anthracene
Fluorine
  Inorganic derivatives
    Hydrogen fluoride
  Aliphatic derivatives
    Fluoro compounds
  Pseudoaromatic derivatives
  Aromatic derivatives
  Pseudoaromatic rings
  Aromatic rings
Chlorine, Bromine, Iodine
Oxygen
  Inorganic derivatives
    Water
    Hypochlorous acid
    Hydrogen peroxide
  Aliphatic derivatives
    Alcohols
    Ethers
    Oxonium ions
    Unicovalent oxygen cations
    Aldehydes
    Ketones
    Carboxylic acids (carbonic acid is defined as containing two carboxylic-acid groups)
    Hypochlorites
    Peroxides
  Pseudoaromatic derivatives
  Aromatic derivatives
  Pseudoaromatic rings
    Furan
    Benzofuran
    Dibenzofuran
  Aromatic rings
    Pyrylium
    Benzopyrylium
    Xanthylium
Sulfur
  Inorganic derivatives
    Hydrogen sulfide
    Sulfoxylic acid

[10] We have included certain classes and functional units which are hypothetical except in secondary divisions. Obviously, pseudoaromatic and aromatic derivatives imply the presence of pseudoaromatic or aromatic rings. These rings may well take precedence over the derivative in fixing the gross position of the compound in the system. The derivative then fixes the more specific location of the compound.

- Sulfurous acid
- Thionyl chloride
- Sulfuric acid
- Hydrogen disulfide
- Aliphatic derivatives
- Thiols
- Thioethers
- Sulfonium ions
- Unicovalent sulfur cations
- Sulfoxides
- Sulfinic acids
- Sulfones
- Sulfonic acids
- Polysulfides
- Pseudoaromatic derivatives
- Aromatic derivatives
- Pseudoaromatic rings
- Thiophene
- Thianaphthene
- Aromatic rings
- Thiapyrylium
- Thiaxanthylium

Nitrogen

- Inorganic derivatives
- Ammonia
- N-monohaloamines
- Hydroxylamine
- Nitrous acid
- Nitric acid
- Hydrazine
- Hydrazoic acid
- Aliphatic derivatives
- Amines
- Quaternary ammonium ions
- Dicovalent nitrogen cations
- N-monohaloamines
- Hydroxylamines
- Nitroso compounds
- Nitro compounds
- Compounds containing nonhydrolyzable N—S linkage
- Hydrazines
- Azo compounds
- Azoxy compounds
- Triazeno compounds
- Triazo compounds
- Diazonium ions
- Pseudoaromatic derivatives
- Aromatic derivatives
- Pseudoaromatic rings
- Pyrrole
- Indole
- Isoindole
- Carbazole
- Oxazole
- Isoxazole
- Benzoxazole
- Thiazole
- Benzothiazole
- Naphthothiazoles[11]
- Dithiazoles
- Imidazole
- Pyrazole
- Benzimidazole
- Isoindazole
- Naphthimidazoles
- Naphthopyrazoles
- Oxadiazole
- Benzoxadiazole
- Triazoles
- Benzotriazoles
- Tetrazoles
- Aromatic rings containing one nitrogen
- Pyridine
- Pyrrocolinium
- Quinoline
- Isoquinoline
- Benzo[*h*]quinoline
- Benzo[*f*]quinoline
- Benzo[*g*]quinoline
- Phenanthridine
- Acridine
- Aromatic rings containing one nitrogen fused with (*a*) pseudoaromatic and (*b*) aromatic rings containing oxygen
- Aromatic rings containing one nitrogen fused with (*a*) pseudoaromatic and (*b*) aromatic rings containing sulfur
- Aromatic rings containing one nitrogen fused with pseudoaromatic rings containing nitrogen
- Aromatic rings containing one nitrogen fused with other aromatic rings containing one nitrogen
- Aromatic rings containing one nitrogen and one or more oxygen atoms
- Phenazoxonium
- Aromatic rings containing one nitrogen and one or more sulfur atoms
- Phenazathionium
- Aromatic rings containing two nitrogens
- Pyrimidine
- Pyrazine
- Pyridazine
- Quinazoline
- Quinoxaline
- Cinnoline
- Phthalazine
- Aromatic rings containing two nitrogens fused with other functional heterocyclic rings
- Aromatic rings containing two nitrogens and other hetero atoms
- Aromatic rings containing three nitrogens
- *s*-Triazine
- *as*-Triazine
- Benzotriazines
- Aromatic rings containing three nitrogens fused with other functional heterocyclic rings
- Aromatic rings containing three nitrogens and other hetero atoms
- Aromatic rings containing four or more nitrogens
- *Foreign elements*[12] arranged in order of increasing atomic numbers. To illustrate the arrangement of compounds under a particular foreign element, the system for filing under arsenic is outlined here.

Arsenic

- Inorganic derivatives
- Arsine
- Arsenic cations[13] (in order of increasing oxidation state)
- Monohaloarsenic compounds
- Arsenic-oxygen bonds (in order of increasing oxidation state)
- Arsenic-arsenic bonds
- Aliphatic derivatives
- Arsines
- Arsonium ions
- Monohaloarsenic compounds
- Arsenic-oxygen bonds

R_2AsOH

$R_3\overset{+}{A}s—O^-$

$R—As{=}O$

$R—As(OH)_2$ files as $R—As{=}O + H_2O$

$R_2\overset{+}{A}s—OH$ (|) O^-

$R—As(OH)_2$ (|) O^-

- Compounds containing nonhydrolyzable As—S bonds
- Compounds containing nonhydrolyzable As—N bonds
- Arsenic-arsenic bonds
- Pseudoaromatic derivatives
- Aromatic derivatives
- Pseudoaromatic rings
- Arsenole
- Aromatic rings
- Arsenine
- Arsinoline

[11] The plural denotes that there may be several isomeric rings. Each individual ring, however, is filed as a separate functional unit.

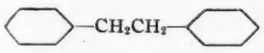
[12] Elements other than hydrogen, carbon, the halogens, oxygen, sulfur, nitrogen, lithium, sodium, potassium, magnesium, and calcium.

[13] The category of inorganic cations is of value only in the case of those foreign elements which form salts containing the foreign element as a cation.

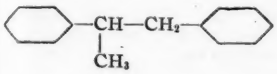
These tables are pages selected from "A Survey of Antimalarial Drugs, 1941–1945."[3] They illustrate the orientation of individual structures as well as their order of appearance in the Survey system.

Table 1 comprises the last compounds falling in the division *Carbon* down through the first compounds falling in the division *Chlorine*. SN 15,146 and SN 15,147 both contain two identical functional units; SN 15,147 follows SN 15,146 because it has a larger number of carbon atoms. SN 11,078 contains a new functional unit, naphthalene, in the same class and division. SN 4603 contains, in addition to a naphthalene nucleus, a second functional unit, benzene, and therefore follows SN 11,078. SN 4600 contains a new functional unit, phenanthrene. SN 15,292 opens the fluorine division and SN 4 opens the chlorine division. SN 12,750, SN 10,342, and SN 15,148 are aliphatic chloro compounds; the latter contains two functional units and hence falls last.

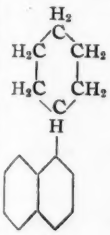
TABLE I



SN 15,146. $C_{14}H_{14}$. *bibenzyl*

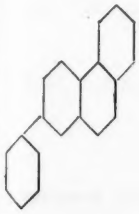


SN 15,147. $C_{15}H_{16}$. *α*-methyl*bibenzyl*



SN 11,078. $C_{16}H_{18}$. 1-cyclohexyl*naphthalene*

SN 4603. $C_{16}H_{10}$. *fluoranthene*



SN 4600. $C_{20}H_{14}$. 2-phenyl*phenanthrene*

HF — SN 15,292. HF. *hydrofluoric acid*

HCl — SN 4. HCl. *hydrochloric acid*

$(CH_3)_3C—Cl$ — SN 12,750. C_4H_9Cl. 2-chloro-2-methyl*propane*

$CH_3—(CH_2)_{11}—Cl$ — SN 10,342. $C_{12}H_{25}Cl$. 1-chloro*dodecane*

$Cl—CH_2CH_2—Cl$ — SN 15,148. $C_2H_4Cl_2$. 1,2-dichloro*ethane*

Table 2 comprises the first compounds falling in the division *Oxygen*. SN 3 and SN 14,466 are in the class *Inorganic derivatives*. The remainder are aliphatic alcohols. Note that alicyclic rings play no role as rings in determining the position in the Survey system.

TABLE 2

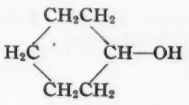
H_2O — SN 3. H_2O. *water*

$HBrO_3$ — SN 14,466. $HBrO_3$. *bromic acid*

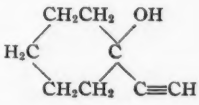
$C_2H_5—OH$ — SN 9592. C_2H_6O. *ethyl alcohol*

$(CH_3)_2CH—OH$ — SN 3473. C_3H_8O. *isopropyl alcohol*

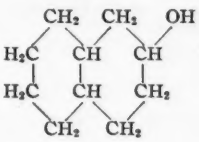
$(CH_3)_3C—OH$ — SN 12,794. $C_4H_{10}O$. *tert-butyl alcohol*



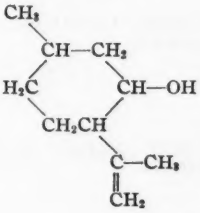
SN 15,109. $C_6H_{12}O$. *cyclohexanol*



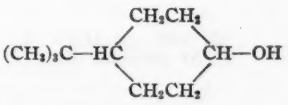
SN 3389. $C_8H_{12}O$. 1-ethynyl*cyclohexanol*



SN 3443. $C_{10}H_{18}O$. decahydro-*2-naphthol*

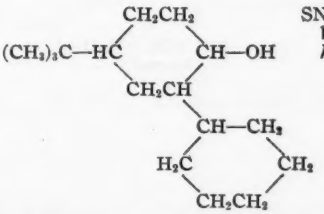


SN 11,967. $C_{10}H_{18}O$. *isopulegol*

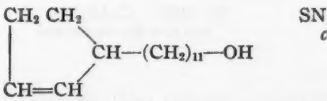


SN 7842. $C_{10}H_{20}O$. 4-*tert*-butyl*cyclohexanol*

$CH_3—(CH_2)_{11}—OH$ — SN 8197. $C_{12}H_{26}O$. *dodecyl alcohol*



SN 7843. $C_{16}H_{30}O$. 4-*tert*-butyl - 2 - cyclohexyl*cyclohexanol*



SN 3406. $C_{16}H_{30}O$. *hydrocarpyl alcohol*

$CH_3—(CH_2)_9—CH(OH)—(CH_2)_5—CH_3$ SN 8188. $C_{17}H_{36}O$. *7-heptadecanol*

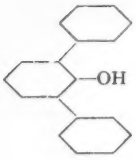
Table 3 comprises part of a series of compounds in which the principal functional unit is an aromatic hydroxyl group. Note that SN 4599 is a tautomer of 9-phenanthrol and is classified with that compound.

Table 4 comprises a wide variety of structures brought together because the principal functional unit is the inorganic hydrogen sulfide.

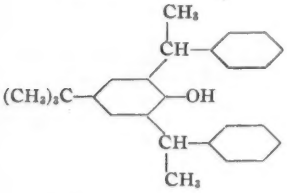
Table 5 comprises part of a series of compounds containing but one functional unit, an aliphatic amino group.

Table 6 comprises part of a series of compounds containing (1) an aliphatic amino group, (2) an aliphatic hydroxyl group, (3) an aromatic bromo group, and (4) a benzene ring.

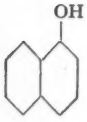
TABLE 3



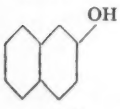
SN 12,821. $C_{18}H_{14}O$. 2,-6-diphenyl*phenol* .



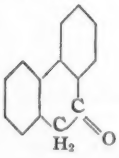
SN 15,097. $C_{26}H_{30}O$. 4-*tert* - butyl - 2,6 - bis-(α - methylbenzyl)-*phenol*



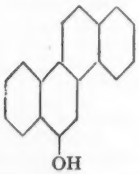
SN 10,402. $C_{10}H_8O$. *1-naphthol*



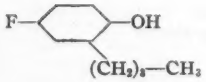
SN 3011. $C_{10}H_8O$. *2-naphthol*



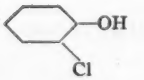
SN 4599. $C_{14}H_{10}O$. *9-(10)-phenanthrone*



SN 4636. $C_{18}H_{12}O$. *6-chrysenol*



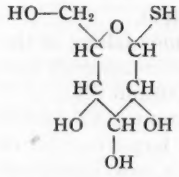
SN 2297. $C_{10}H_{13}FO$. 2-butyl-4-fluoro*phenol*



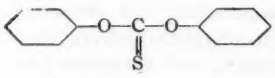
SN 14,420. C_6H_5ClO. *o*-chloro*phenol*

TABLE 4

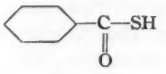
H_2S SN 15,021. H_2S. *hydrogen sulfide*



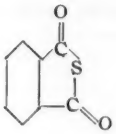
SN 395. $C_6H_{12}O_5S$. 1-thio-*glucose*



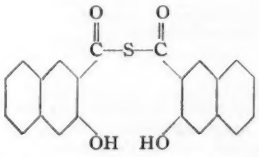
SN 2853. $C_{13}H_{10}O_2S$. thiono-*carbonic acid*, diphenyl ester



SN 3195. C_7H_6OS. thio*benzoic acid*



SN 10,376. $C_8H_4O_2S$. *isothianaphthene-1,3-dione*



SN. 7223. $C_{22}H_{14}O_4S$. 3-hydroxythiol - *2 - naphthoic acid*, anhydride

CS_2 SN 13,970. CS_2. *carbon disulfide*

$CH_3—O—C(=S)—SH$ SN 3197. $C_2H_4OS_2$. *methylxanthic acid*

$C_2H_5—O—C(=S)—SH$ SN 3198. $C_3H_6OS_2$. *xanthic acid*

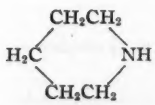
$(CH_3)_2CH—O—C(=S)—SH$ SN 14,939. $C_4H_8OS_2$. *isopropylxanthic acid*

$CH_3CH_2—CH(CH_3)—O—C(=S)—SH$ SN 5229. $C_5H_{10}OS_2$. *sec-butylxanthic acid*

$(CH_3)_2CH—CH_2—O—C(=S)—SH$ SN 14,942. $C_5H_{10}OS_2$. *isobutylxanthic acid*

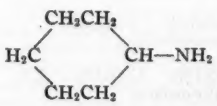
$CH_3—(CH_2)_3—O—C(=S)—SH$ SN 9662. $C_5H_{10}OS_2$. *butylxanthic acid*

TABLE 5



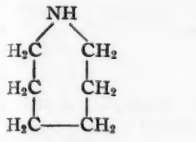
SN 2654. $C_5H_{11}N$. *piperidine*

$CH_3—(CH_2)_4—NH_2$ SN 15,282. $C_5H_{13}N$. *amylamine*

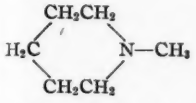


SN 14,413. $C_6H_{13}N$. *cyclohexylamine*

TABLE 5 (*Continued*)



SN 14,611. $C_6H_{13}N$. *hexamethylenimine*

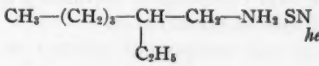


SN 2651. $C_6H_{13}N$. 1-methyl*piperidine*

$(CH_3CH_2CH_2)_2NH$ SN 14,612. $C_6H_{15}N$. *dipropylamine*

$(C_2H_5)_3N$ SN 11,075. $C_6H_{15}N$. *triethylamine*

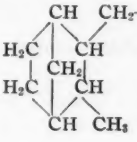
$CH_2{=}CH{-}CH_2{-}N(C_2H_5)_2$ SN 11,951. $C_7H_{15}N$. N,N-diethyl*allylamine*



SN 14,333. $C_8H_{19}N$. 2-ethyl*hexylamine*

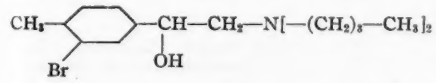
$[(CH_3)_2CH{-}CH_2{-}]_2NH$ SN 15,283. $C_8H_{19}N$. *diisobutylamine*

$[CH_3{-}(CH_2)_3{-}]_2NH$ SN 10,172. $C_8H_{19}N$. *dibutylamine*

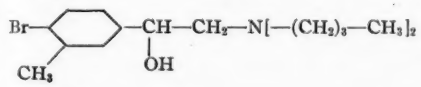


SN 9010. $C_9H_{17}N$. 3-methyl-*2-norcamphanemethylamine*

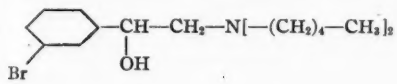
TABLE 6



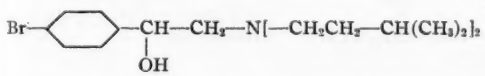
SN 8928. $C_{17}H_{28}BrNO$. 3-bromo-α-(dibutylaminomethyl)-4-methyl*benzyl alcohol*



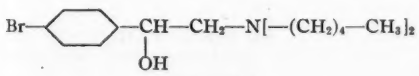
SN 8416. $C_{17}H_{28}BrNO$. 4-bromo-α-(dibutylaminomethyl)-3-methyl-*benzyl alcohol*



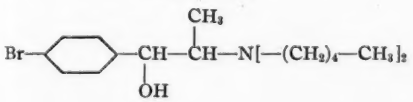
SN 8124. $C_{18}H_{30}BrNO$. *m*-bromo-α-(diamylaminomethyl)*benzyl alcohol*



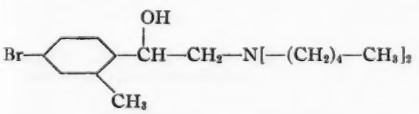
SN 8933. $C_{18}H_{30}BrNO$. *p*-bromo-α-(diisoamylaminomethyl)*benzyl alcohol*



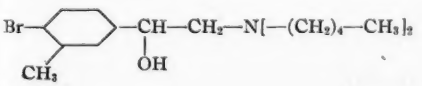
SN 4911. $C_{18}H_{30}BrNO$. *p*-bromo-α-(diamylaminomethyl)*benzyl alcohol*



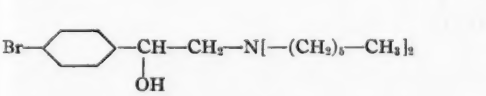
SN 6657. $C_{19}H_{32}BrNO$. *p*-bromo-α-(1-diamylaminoethyl)*benzyl alcohol*



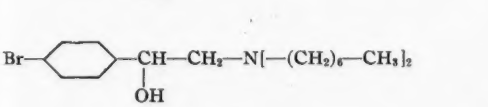
SN 8504. $C_{19}H_{32}BrNO$. 4-bromo-α-(diamylaminomethyl)-2-methyl-*benzyl alcohol*



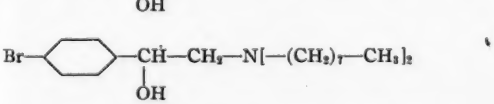
SN 6651. $C_{19}H_{32}BrNO$. 4-bromo-α-(diamylaminomethyl)-3-methyl-*benzyl alcohol*



SN 8396. $C_{20}H_{34}BrNO$. *p*-bromo-α-(dihexylaminomethyl)*benzyl alcohol*



SN 8300. $C_{22}H_{38}BrNO$. *p*-bromo-α-(diheptylaminomethyl)*benzyl alcohol*



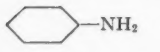
SN 8367. $C_{24}H_{42}BrNO$. *p*-bromo-α-(dioctylaminomethyl)*benzyl alcohol*

Table 7 comprises the first members of the aromatic amines.

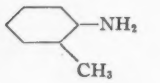
Table 8 comprises the first compounds containing a quinoline ring as the principal functional unit.

Table 9 comprises several compounds related to sulfadiazine. The pyrimidine nucleus is the principal functional unit followed, in turn, by (2) an aromatic amine, (3) an aromatic amine, (4) an aromatic sulfonic acid, and (5) a benzene ring.

TABLE 7

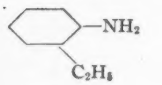


SN 177. C_6H_7N. *aniline*

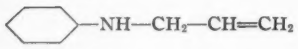


SN 12,911. C_7H_9N. *o-toluidine*

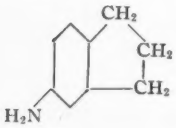
SN 4037. C_7H_9N. *p-toluidine*



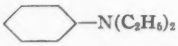
SN 12,912. $C_8H_{11}N$. *o-*ethyl*aniline*



SN 11,100. $C_9H_{11}N$. *N-*allyl*aniline*

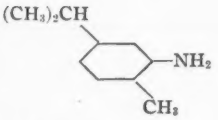


SN 9239. $C_9H_{11}N$. *5-indanamine*

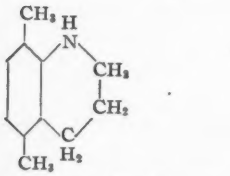


SN 11,939. $C_{10}H_{15}N$. *N,N-*diethyl*aniline*

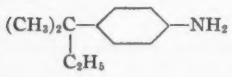
SN 7799. $C_{10}H_{15}N$. *p-tert-*butyl*aniline*



SN 1654. $C_{10}H_{15}N$. *carvacrylamine*

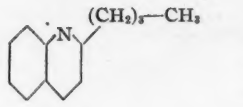


SN 2967. $C_{11}H_{15}N$. 1,2,3,4 - tetrahydro - 5,8-dimethyl*quinoline*

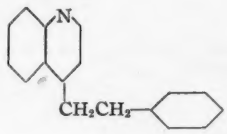


SN 12,062. $C_{11}H_{17}N$. *p-tert-*amyl*aniline*

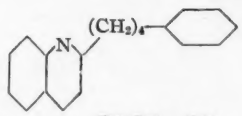
TABLE 8



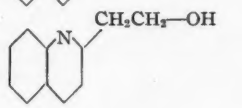
SN 6701. $C_{13}H_{15}N$. 2-butyl*quinoline*



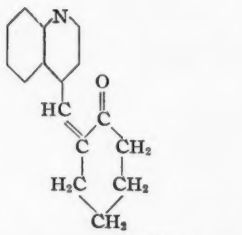
SN 8598. $C_{17}H_{15}N$. 4-phenethyl*quinoline*



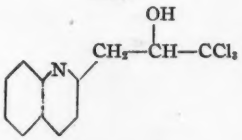
SN 8817. $C_{19}H_{19}N$. 2-(4-phenylbutyl)*quinoline*



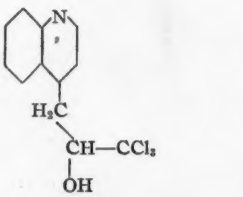
SN 654. $C_{11}H_{11}NO$. *2-quinolineethanol*



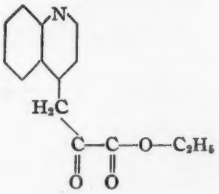
SN 10,009. $C_{16}H_{15}NO$. 2-(4-quinolylmethylene)*cyclohexanone*



SN 82. $C_{12}H_{10}Cl_3NO$. *α-*(trichloromethyl) - *2* - *quinolineethanol*

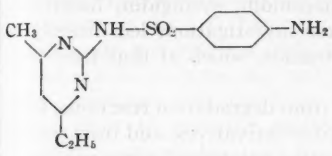


SN 13,645. $C_{12}H_{10}Cl_3NO$. *α-*(trichloromethyl) - *4* - *quinolineethanol*

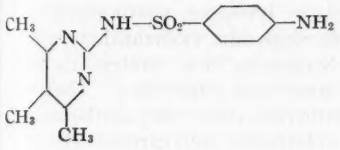


SN 961. $C_{14}H_{13}NO_3$. *4-quinolinepyruvic acid*, ethyl ester

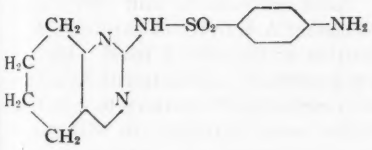
TABLE 9



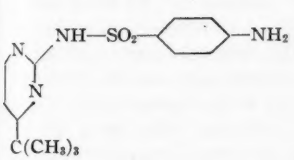
SN 7505. $C_{13}H_{16}N_4O_2S$. N^1-(4-ethyl-6-methyl-2-pyrimidyl)*sulfanilamide*



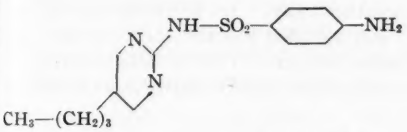
SN 5240. $C_{13}H_{16}N_4O_2S$. N^1-(4,5,6-trimethyl-2-pyrimidyl)*sulfanilamide*



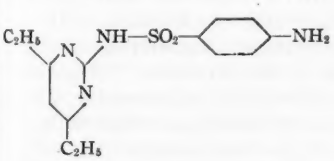
SN 1499. $C_{14}H_{16}N_4O_2S$. N^1-(5,6,7,8-tetrahydro-2-quinazolyl)*sulfanilamide*



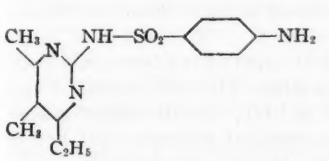
SN 5284. $C_{14}H_{18}N_4O_2S$. N^1-(4-*tert*-butyl-2-pyrimidyl)*sulfanilamide*



SN 943. $C_{14}H_{18}N_4O_2S$. N^1-(5-butyl-2-pyrimidyl)*sulfanilamide*



SN 7160. $C_{14}H_{18}N_4O_2S$. N^1-(4,6-diethyl-2-pyrimidyl)*sulfanilamide*



SN 7159. $C_{14}H_{18}N_4O_2S$. N^1-(4-ethyl-5,6-dimethyl-2-pyrimidyl)*sulfanilamide*

Paul Karrer

RALPH E. OESPER

University of Cincinnati, Cincinnati, Ohio

PAUL Karrer, the son of Swiss parents, was born in Moscow on April 21, 1889. The family returned to their homeland in 1892. After finishing the course at the Gymnasium in Aarau in 1908, the promising youth entered the University of Zurich, primarily to study chemistry. He was trained principally by Alfred Werner,[1] under whose guidance he completed his doctorate dissertation, "Die Nitrosopentammin-kobaltsalze." During 1912–13 he acted as lecture assistant to Werner and also began his fruitful career as an independent investigator. His studies of organic arsenic compounds brought him into correspondence with Paul Ehrlich, then director of the "Georg Speyer Haus" in Frankfurt. Karrer went to this chemotherapeutic research institute in 1913 as Ehrlich's collaborator and later was appointed a full member of the staff. Numerous papers on organic arsenic derivatives are the tangible record of this period. Among these was his study of the salvarsan-metal complex salts, of which silver salvarsan was introduced into therapeutical practice.

In 1918 Karrer was recalled to his alma mater as extraordinary professor of organic chemistry. The next year he succeeded Werner (d. November 15, 1919) as professor of chemistry and director of the *Chemisches Institut* (chemistry department).

The first major field of research during this period of Karrer's work comprised sugars and polysaccharides (starches, glycogen, inulin, cellulose, lichenin, chitin). The enzymatic splitting of chitin, lichenin, and cellulose was discovered and thoroughly studied. New methods of preparing anhydrosugars were developed, and additional members of this class of compounds were discovered. A special procedure resulted in the amination of cellulose, and this led in turn to the preparation of amino yarn, which gave new insights into the nature of dyeing processes. The studies on polysaccharides were compiled in a monograph "Polymere Kohlenhydrate," published at Leipzig in 1925.

Studies of glucosides, tannins, and lecithins were carried out parallel to the foregoing. The inhomogeneity of the tannins was revealed, the first crystallized tannins were prepared, and it was shown that the natural lecithins consist of mixtures of α- and β-lecithins. Numerous papers were devoted to the configuration of the albumin amino-acids and related compounds. It was proved that all albumin amino-acids belong to the same steric series, and that the simple alkaloids (nicotine, stachydrine, etc.) have the same configuration.

In 1926 Karrer began his extended studies of plant pigments. The anthocyanins were found to be mixtures, and new examples of these compounds were discovered. The constitution of certain imperfectly known anthocyanidines, such as paeonidin, syringidin, hirsutidin, was determined. These investigations led directly to the study of the carotenoids, which at that time were only slightly known.

Information gained from degradation reactions, from syntheses of the perhydro-derivatives, and from partial syntheses of the respective carotenoid pigments themselves, provided the basis for working out the constitution of α- and β-carotene, lycopene, xanthophyll, crocetin, bixin, astacin, flavoxanthin, violaxanthin, citraurin, and squalene. Numerous new carotenoids were discovered and their structures unravelled. These included zeaxanthin, antheraxanthin, chrysanthemaxanthin, auroxanthin, torularhodin, and carotenoids, such as rhodoviolascin, rhodoxanthin, etc., obtained from purple bacteria. After Steenbock and von Euler demonstrated the vitamin A activity of carotene, Karrer turned his attention to vitamin A itself. He succeeded in isolating this material, elucidated its structure, and worked out its constitutional relations to carotene.

His vitamin studies were extended to vitamin C (ascorbic acid), riboflavin (vitamin B_2), vitamin E, vitamin K, nicotinamide, and vitamin A_2. In 1934 Karrer succeeded, by means of degradation processes and by its synthesis, in clearing up the structure and constitution of riboflavin. Numerous similar compounds of the flavin group were synthesized in his laboratory. Other triumphs included the first synthesis (1938) of α-, β-, and γ-tocopherol, *i. e.*, vitamin E. The vitamin E field was also extended synthetically. In 1939 vitamin K (α-phylloquinone) was isolated in pure form for the first time. Researches in the period 1941 to 1943 contributed greatly to the clarification of the constitution of vitamin A_2.

Another field of Karrer's researches dealt with the codehydrases (cozymase and codehydrase). It was demonstrated that the hydrogen transferring agency of both these coferments is nicotinamide. Its pyridine nitrogen carries a phosphorylated sugar residue, and in this form it can take up two hydrogen atoms with production of an ortho dihydro compound of the amide. An insight was thus gained into the mechanism of the dehydrogenation processes brought about by the codehydrases.

Most of Karrer's 640 papers have been published in the *Helvetica Chimica Acta*. His well-known "Organic Chemistry" appeared in 1927; the 9th edition was published in 1943. This excellent reference text has been translated into English, Italian, and Spanish.

Professor Karrer's achievements have been given the recognition they so richly merit. He holds honorary degrees from Breslau, Basle, Lausanne, Zurich, Lyons, Paris, and Sofia. He was awarded the Marcel Benoist Prize (Switzerland) and the Cannizzaro Prize (Rome). The Nobel Prize for 1937 was equally divided between W. N. Haworth "for his research on carbohydrates and vitamin C" and Paul Karrer "for his investigations of carotenoids and flavins and for his research on vitamins A and B_2."

[1] PFEIFFER, P., THIS JOURNAL, 5, 1090–8 (1928).

On Heats of Solution

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THE teaching of heat effects accompanying solution is generally confined to a very short time during the first course in physical chemistry. As a result students generally do not obtain a feeling for the principles involved nor do they see any connection with the usual ideas associated with the heats of chemical reaction. In an effort to give the matter greater clarity, the following approach has been used by the author. He believes the method to be novel, although it is implied in some discussions of the material. It might well be, since correct discussions must have a common basis in the fundamental law of Hess.

A concept necessary to this approach is that of the "mol-unit of solution." This quantity is defined as that amount of solution containing one mol of the active or significant ingredient. Thus when one mol of sulfuric acid is mixed with 20 mols of water, the resulting quantity of solution is a mol-unit of that particular solution. If, however, the same concentration is prepared by mixing one-half mol of the acid with ten mols of water, the resulting quantity is one-half of a mol-unit of the same kind of solution. A further designation is necessary in order to identify completely the solution, since the term "mol-unit" defines quantity but not concentration. Mol-fraction or some other designation might be used without difficulty.

The advantage of adopting this concept lies in that the integral heat of solution[1] may then be used in a manner similar to that using heats of formation. The integral heat of solution may in fact then be considered the heat of formation of the solution with respect to the pure components. For the formation of one mol-unit of a solution containing two mols of water per mol of sulfuric acid, we may write an equation,

$$H_2SO_4 + 2H_2O \rightarrow (H_2SO_4 + 2H_2O);\ \Delta H_2 = -9400 \text{ cal.}$$

where the parentheses enclose the components of the solution formed. The subscript on the ΔH refers to the fact that the heat change quoted is the integral heat of solution for a mol-unit containing two mols of water. The convenience of this notation will become evident in the examples to be given.

When the idea herein explained is once grasped, a good many dilution, solution, and mixing heats may be computed with ease. A few examples are offered below.

1. The heat effect of dissolving two mols of sulfuric acid in four mols of water.

$$2H_2SO_4 + 4H_2O \rightarrow 2(H_2SO_4 + 2H_2O);\ \Delta H = 2\Delta H_2 = -18{,}800 \text{ cal.}$$

Notice that this is just the formation of two mol-units of the same solution as used in the introductory example. As such, the heat effect must be twice that of the former.

2. The heat effect of mixing two mols of water with a solution containing one mol of sulfuric acid and two mols of water.

$$2H_2O + (H_2SO_4 + 2H_2O) \rightarrow (H_2SO_4 + 4H_2O)$$

In this example the convenience of the subscript notation on the ΔH's becomes evident as well as the analogy to the use of the more usual heats of formation. The heat of a reaction is equal to the sum of heats of formation for the products minus that sum for the reactants. Integral heats of solution may now be substituted for heats of reaction when the "reaction" is of the type here considered, and

$$\Delta H = \Delta H_4 - \Delta H_2$$

$$\Delta H = -12{,}300 - (-9400) = -2900 \text{ cal.}$$

Note that the two mols of water on the left of the arrow have no heat of solution in this regard since they represent one of the pure components, corresponding to elements in standard states for the analogous case of heats of formation.

That the equation written for the ΔH of the reaction is correct can be seen by application of the law of Hess. Thus,

$$H_2SO_4 + 4H_2O \rightarrow (H_2SO_4 + 4H_2O);\ \Delta H_4 = -12{,}300 \text{ cal.}$$

$$H_2SO_4 + 2H_2O \rightarrow (H_2SO_4 + 2H_2O);\ \Delta H_2 = -\ 9400 \text{ cal.}$$

whence, by subtraction is obtained

$$2H_2O + (H_2SO_4 + 2H_2O) \rightarrow (H_2SO_4 + 4H_2O);\ \Delta H = \Delta H_4 - \Delta H_2$$

3. The heat effect of mixing two different solutions.

$$(H_2SO_4 + 2H_2O) + (H_2SO_4 + 4H_2O) \rightarrow 2(H_2SO_4 + 3H_2O)$$

$$\Delta H = 2\Delta H_3 - \Delta H_4 - \Delta H_2$$

$$\Delta H = 2(-11{,}700) - (-12{,}300) - (-9400) = -700 \text{ cal.}$$

In this kind of problem the analogy to heats of formation is quite obvious.

4. Heat effect due to solution when a chemical reaction is being considered.

$$(H_2SO_4 + 6H_2O) + 2(NaOH + 6H_2O) \rightarrow (Na_2SO_4 + 20\ H_2O);\ \Delta H = ?$$

The heat effect here can be computed in two parts, that for the reaction and that for solution. The heat effect for the reaction is computed from the usual heats of formation of the *pure compounds, i. e.*, for

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O;\ \Delta H_I$$

the heat effect involving solution can be computed as

$$\Delta H_{II} = \Delta H_{20}\,(Na_2SO_4) - \Delta H_6(H_2SO_4) - 2\Delta H_6(NaOH)$$

where now parentheses have been used to enclose the formula of the compound whose integral heat of solution is being indicated. The heat effect of the original reaction is now

[1] LEWIS, G. N., AND M. RANDALL, "Thermodynamics," McGraw-Hill Book Company, Inc., New York, 1923, p. 89.

$$\Delta H = \Delta H_I + \Delta H_{II}$$

A similar method is used if water is one of the reactants rather than one of the products. This latter type of example may be checked by recourse to the law of Hess as previously indicated for a simpler example.

It is believed that this method, when mastered, leads to greater facility in computing heat effects in solution. Introduction to the method should not prove too difficult if it is undertaken immediately after treating the usual heats of formation.

Friedrich Fichter

RALPH E. OESPER

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THE Swiss are an intelligent, industrious, self-reliant, effective people. These same admirable qualities are displayed in their universities and polytechnic schools, where chemical education and original research are kept at a notably high level. It is the professors, of course, who are directly responsible for this record. The Swiss schools have always had competent occupants of the chairs of chemistry, and the higher authorities have seen to it that nominations to these posts have gone only to those of whose success there was practically no doubt. The subject of this sketch is an excellent illustration of the results of this system of picking a promising man and then giving him adequate support.

FRIEDRICH FICHTER

Friedrich Fichter, the son of a manufacturer of silk ribbons, was born on July 6, 1869. From 1888 to 1890 he attended the University of Basle, and then transferred to the University of Strasbourg for more specialized training. Here he came under the influence of Rudolf Fittig, who made the young Swiss his assistant in 1893. The doctorate was awarded in 1894. Fichter's real life-work began in 1895, when he returned to Basle as assistant to J. Piccard. In 1896 he habilitated as Privatdozent, was promoted to an extraordinary professorship in 1903, and in 1912 was made full professor and head of the inorganic division. He occupied this position until his retirement in 1939.

Almost 300 papers have come from his laboratory,

PROFESSOR FICHTER DEMONSTRATING THE BURNING OF ALUMINUM POWDER

and a long succession of young chemists have worked under his guidance. Quite a few of his papers, including reviews and summaries, have appeared in English, especially in the *Transactions of the Electrochemical Society*. His favorite fields of investigation have been oxidations by means of gaseous fluorine, the preparation of molten beryllium, and, especially, various aspects of organic electrochemistry. His books include "Anleitung zum Studium der chemischen Reaktionen" (4th edition, **1928**), "Übungen in quantitativer chemischer Analyse (2nd edition, **1938**), "Das Verhältnis der anorganischen zur organischen Chemie" (**1933**), and "Organische Elektrochemie" (**1942**).

In 1928 he was guest professor at the University of Birmingham. He served as president of the Union of Swiss Chemical Societies and as vice-president of the International Union of Chemistry. When the *Helvetica Chimica Acta* was begun in 1918, he was elected its editor-in-chief. He still retains this responsible position. In this period the circulation has grown from 500 to about 3000. An open letter, commending his services and signed by the most prominent Swiss chemists, was published in 1943 when the 25th anniversary of the founding of this excellent journal was celebrated.

The Scientific Importance of the Nuclear Power Projects[1]

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This is the first of a series of articles, written by Oak Ridge scientists, on the chemical significance of modern nuclear science and technology.

FOR five years the governments of the United States, Great Britain, and Canada pressed in greatest secrecy a group of enormous war projects with the goal of producing the most devastating explosives possible, explosives releasing the stored up energy of the nuclei of atoms. A large fraction of research and almost all of the technological work was carried out in the United States. The people of the world, of the United Nations, and of the enemy states received their first knowledge of the existence of these projects with the dramatic evidence of their successful conclusion when it was announced on August 6, 1945, that the first atomic bomb had annihilated the city of Hiroshima, Japan.

A relatively small number of research workers and academic, industrial, and military administrators were informed of the significance of their tasks from the time of their employment on the project. Because of the magnitude of the job, however, this number is probably several thousand. Many of these workers are now returning to academic research and teaching, and they will bring with them a body of technical knowledge and point of view that will revolutionize the research concepts of their associates and students.

It is the purpose of this and several subsequent articles to foster in a general manner an appreciation of the accomplishments of the projects and the background of factual knowledge from which they started, as a body of self-consistent science, and to emphasize the significance of the highly specialized advances to the chemists of the United States.

The work on the Nuclear Power Projects has established an everyday significance for many methods that formerly were only specialized techniques on a small scale for nuclear physics and has made available in gram or kilogram amounts many materials that were never thought to be available in separate form. It has made abstract concepts in physics, chemistry, and engineering become real. It has produced technical problems on a scale approaching the fantastic, and the staffs have worked out solutions to those problems that give techniques and know-how that will help solve many other problems of modern science.

The success of the Projects has also given the world a political problem of undreamed of proportions in the military significance of the atomic bomb, and this bomb has simultaneously given the people of the world a compelling reason to reconsider the basis of international cooperation and the conditions necessary for the existence of the civilization we now know. The prospects of the almost instantaneous elimination of all of our metropolitan centers in a night of terror are to be considered by our national and international leaders together with the prospects of increasing the health, comfort, and grace of human life in all nations by virtue of the scientific advances made possible by separated isotopes and by the energy of fission.

Surely the scientists of the Nuclear Power Projects have given the world Pandora's Box. The discovery and development of power or knowledge in concentrated form has always presented mankind with such a problem. In this respect the ultimum has probably been reached in the advance made in the amount of power available to man. It is unlikely that so much advance in the amount of knowledge will be held within the confines of secrecy, so the increment of knowledge may also be an ultimum for the world.

RELEASE OF INFORMATION

The success of the world in accommodating to the social and technological impact of atomic bombs and nuclear science and technology will be aided by the diffusion of knowledge about the general accomplishments of the Nuclear Power Projects. In this regard the War Department and President Truman made a commendable start in the publication of the official Smyth Report, "Atomic Energy for Military Purposes" (*1*). The best description of the explosion of an atomic bomb that has appeared to date is that of William Lawrence on the New Mexico test of July 16, 1945 (*2*). Since early September, 1945, there has been a fair volume of release of official information in the form of approved speeches and journal articles, but there has been no single authoritative vehicle. At the present date each of the major units of the Projects is preparing reports of the work in the hope that a major part of these dealing with advances in basic science and technology can receive open publication when the organization of the national program has achieved clarity and stabilization.

A number of bills has been introduced in the House and Senate of the Congress of the United States for the

[1] Note on terminology: We are in hearty agreement with the editors of THIS JOURNAL in hoping that the inadequate term "atomic energy" will not be adopted in scientific terminology. The contest seems already lost in many quarters, however, and we consider it only good sportsmanship to use the term "atomic bomb" when referring to the military application.

purpose of ordering the national and international aspects of atomic energy. The Senate has established a Special Committee on Atomic Energy under the chairmanship of Senator Brien McMahon of Connecticut.[2] The McMahon Committee has held a series of hearings on the significance of the atomic power projects, the promise of further developments in the field, together with the features of government legislation that may be needed for proper support and control in the national interest. The major results of hearings and action are reported in the press and current scientific journals and will be covered elsewhere in the JOURNAL OF CHEMICAL EDUCATION. By the time this article is published it is probable that the Congress will have passed a bill covering the domestic aspects of control and development of nuclear technology.

GENERAL DISCUSSION

This is the first of several articles being written by members of the research groups of the three major units located at Oak Ridge, Tennessee, one of the four cities[3] built secretly for the personnel associated with the atomic bomb production plants. The units are the electromagnetic separation plant for U^{235} operated by the Tennessee Eastman Company, following major research at the University of California; the gaseous diffusion separation plant for U^{235} designed by the Kellex Company and operated by the Carbide and Carbon Chemical Company, following major research at Columbia University; and the Clinton Laboratories, a research unit established by the University of Chicago and now operated by the Monsanto Chemical Company, for pilot work for the Hanford Plant and for research and development work, especially involving plutonium, the fission products, and work at an operating pile. The Fercleve Company formerly operated a plant for the separation of U^{235} by thermal diffusion for which research was done by the Naval Research Laboratories.

Subsequent articles of this series, appearing from time to time, will present the scientific background of certain fields of endeavor of the projects and give as general a picture of the techniques and accomplishments as security regulations permit. Brief sketches of the fields of nuclear reactions, nuclear energetics, isotope fractionation, electromagnetic isotope separation, nuclear fission, isotope chemistry, and the special chemistry of some project materials are given in the remainder of this article.

Since 1919 a large number of artificial nuclear reactions have been developed. Those involving charged particles have been carried out with cyclotrons, Van de Graaff and other accelerators, and have only been carried out on the microgram or the curie scale.[4] Some of these reactions produce neutrons which in turn can be used to produce a useful group of nuclear reactions, the most dramatic of which is the fission of the very heavy isotopes (*e. g.*, Th^{232}, U^{235}, U^{238}, Pu^{239}). The production of a multiplying chain reaction in piles based on the fission of U^{235} in uranium and the slowing down of the secondary neutrons have made milligram and gram amounts of neutrons available per day, to produce gram or better amounts of radioactive isotopes per day. The products of many types of nuclear reactions may soon be expected to be articles of chemical commerce.

There exist in nature 273 stable isotopes (presumably all that can occur), and eight very long-lived radioactive isotopes, three of the latter having long chains of shorter-lived descendants. Systematic exploitation of the various types of artificial nuclear reactions has led to the synthesis of about 370 unstable nuclei with half-lives varying from 0.02 second to many decades. Reasonably straight-forward principles have been established which enable one to predict isotope decay energies as a function of charge Z and mass A.

The discovery of the existence of stable isotopes of many chemical elements led to the efforts of physicists to fractionate these by virtue of differences in diffusibility, even several decades ago. The methods were very successful with the two hydrogen isotopes H^1 (protium) and H^2 (deuterium), and more recently with C^{12} and C^{13} and N^{14} and N^{15}. Methods of gaseous diffusion, thermal diffusion, and centrifugation have been applied in pilot plant scale and in the first two cases, full plant scale, for the separation of U^{235} from U^{238}. Developments may be expected for other isotope sets.

Differential acceleration of beams of gaseous ions, particularly in the presence of magnetic fields, have been used for isotope-analytic purposes (mass spectrograph). The solution of many technical problems has elevated this method to a very promising one for large-scale technology wherein gram quantities of relatively pure isotopes may be obtained in one step.

The greatest amount of energy available from a nuclear reaction that can be carried out on a large scale is that from the fission reaction. When a heavy nucleus undergoes fission, as for instance upon neutron capture, it splits into two lighter fragments plus several neutrons; approximately 200 Mev[5] of energy is liberated, largely as kinetic energy of the fragments.

[2] Membership consists of Senators McMahon (Connecticut) Chairman, Connally (Texas), Johnson (Colorado), Vandenberg (Michigan), Austin (Vermont), Byrd (Virginia), Hart (Connecticut), Hickenlooper (Iowa), Millikin (Colorado), Russell (Georgia), and Tydings (Maryland).

[3] Oak Ridge is the residential area of the Clinton Engineer Works and attained a maximum population of 78,000 in the summer of 1945, but a large fraction of the workers lived in the surrounding communities of Roane, Anderson, and Knox counties, Tennessee. The Hanford Engineer Works in Washington had two cities: Hanford, the construction workers' city which had a population of about 60,000 but is now empty, and Richland for the operating workers, with a population of about 16,000. A city of about 6000 was built adjacent to the research laboratory and bomb assembly plant at Los Alamos.

[4] One curie of material is that amount undergoing 3.70×10^{10} radioactive disintegrations a second (as does one gram of radium), and the exact equation connecting the radioactivity A in curies with the mass m in grams of a substance of half-life of t ½ years of atomic weight M is

$$A = \frac{226}{M} \times \frac{1590}{t_{½}} m \qquad (1)$$

It is seen that 1 microgram of isotope of atomic weight of ~40 and half-life about three days corresponds to ~1 curie.

[5] 1 Mev = one million electron volts of energy per particle undergoing reaction, or 2.3×10^7 kg.-cal./mol.

This reaction can be made to occur controllably in an assemblage known as a pile to give a rich source of power and spare neutrons. If the fissionable material is natural uranium, substantial amounts of Pu^{239} will in addition be synthesized. This reaction can also be made to occur very rapidly, with several materials under carefully controlled conditions, to give the nuclear explosion of the atomic bomb.[6] For either of these systems to undergo self-sustaining (chain reacting) operation, a certain minimum amount of fissionable material (the critical mass) must be present.

It is apparent that separate stable isotopes are available of many elements, and eventually all stable isotopes will be available in separated form. Already radioactive isotopes of all elements are available, and most elements have active isotopes of fairly long half-lives (a few hours up to many years). The increased availability of these isotopes will influence remarkably the course of future chemical research. Techniques of handling and methods of analysis must be considered, and in some cases, such as H^1-H^2-H^3 ($t_{1/2}$ = 25 years) or C^{11} ($t_{1/2}$ = 21 minutes)-C^{12}-C^{13}-C^{14} ($t_{1/2}$ = 25,000 years), there will be competition between the fields of application of stable, short-lived, and long-lived isotopes.

[6] The complete fission of 1 kg. of U^{235} or Pu^{239} gives off the same amount of energy in explosion as does 20,000 tons of TNT (heat of explosion = 200 kg.-cal./mol.)

By virtue of the unique position of the fission reaction and of piles in the field of nuclear technology, fission products will be of great interest and ready availability. Radioactive isotopes of all elements from Zn to Eu are known to occur in fission in number in excess of 150. Many of the elements have at least one isotope with a half-life in excess of 12 hours. Elements 43 and 61 (formerly called Ma and Il) do not occur in nature, but have unstable isotopes produced in fission, and so can be isolated in weighable quantities. By nuclear reactions induced in piles (*3*) or on materials produced in piles, radioactive isotopes of elements 93 (Np), 94 (Pu), 95, and 96 have been produced, and an interesting new transition group is now available for study in which filling of the 6*d* and 5*f* electron shells is intermingled.

Introduction has been made in this article to the great scientific, technological, political, and social implications to the world of the Nuclear Power Projects. These are of such a complex nature and of such far-reaching importance that they deserve further development for the scientific world.

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(2) *Ibid.*, Appendix 6.
(3) FOSTER, L. S., J. CHEM. EDUC., **22**, 620 (1945).

A Condensed Water Collector

H. W. STERNBERG and B. T. FISHER

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WHEN reflux operations are carried out on a steam bath or during a humid day, a large amount of water is condensed on the condenser jacket. Traces of this condensate may pass into the reaction vessel even through a tightly fitting stopper or ground glass joint.

In order to prevent this, a condensed water collector[1] may be attached to the reflux condenser by means of a rubber stopper (Figure 1) or a reflux condenser[1] fitted with a ground glass joint and a condensed water collector (Figure 2) may be used. To our knowledge this condensed water collector was used only in Austrian laboratories and is unknown in this country.

[1] May be ordered from A. A. Pesce, Kennett Square, Pennsylvania.

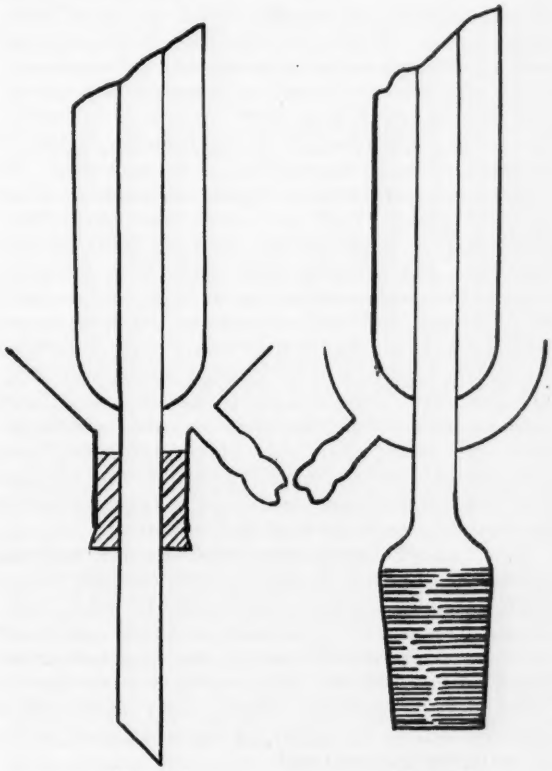

FIGURE 1 FIGURE 2

Training for Technical Report Writing

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JUST how good is scientific writing, in particular chemical writing, at the present time?

Recently there has been some slight awakening of interest in this matter. Some people, at least, are beginning to realize that the quality of the material published in the chemical journals is woefully inadequate. Most frequently the purpose of this material is to report clearly, concisely, and correctly on experimental work in such a manner that a reader skilled in the science can repeat the work and obtain the same results. Of course there are other types of publications, such as presentations of theories, descriptions of apparatus, book reviews, abstracts, topic reviews, textbooks, and patents; however, the reports of experiments far outnumber all the others. Another type of writing important to the chemist is the unpublished technical report; often this is a progress report for his supervisor or a final report dealing with confidential matters.

Through most of his formal education, the student is constantly referred to textbooks which greatly influence his manners of thinking and writing, especially since these textbooks are usually looked up to as being authoritative. What a pity it is that all too often the writers, although they may be masters of their subject, either cannot or do not write in a manner to inspire or help the student to write well! A large proportion of the errors made, especially in the common dashed-off textbook, must be the result of mere carelessness. It requires no careful reading to pick out dozens of errors in many popular freshman college textbooks. Obviously some of these mistakes were not made through ignorance, although some doubt might be expressed in view of the number and nature of them. Of course it is asking too much that all books be free from errors, but surely the number of these errors could be reduced by a little more care in composition and proofreading. It is perturbing to the student to come across such things as incorrect use of nomenclature, notation, and significant figures, just after being admonished about these very things in the classroom. After this kind of training, how can the neophyte chemist be criticized for his inability to express his ideas well in writing?

Some schools still have an unwritten law that the promotion of a staff member to a professorship is partially dependent on the condition that he write a textbook. This practice sometimes introduces such trash into the educational system that our educators should wake up to its effects. Since we have more than an abundance of textbook writers, surely more critical specifications for the quality of textbooks would result in better teaching material.

Many journal articles are written so poorly that several readings are necessary if one is to get at the meaning, and frequently it never appears at all. This condition can be corrected in a large degree by better (maybe "some" is a more appropriate word) training in perspective, organization, grammar, construction, and analysis. The benefits of good writing will appear distinctly if one compares an average article with a well-written one, such as one of the classic Curie reports on radium or the Smyth report on atomic energy.

But perhaps the most atrocious of all chemical writing is found in the unpublished report. Maybe this is because many published reports pass through committees, whereas the author alone contributes to the unpublished ones. This writer has found that in industry he has had, time after time, to teach the basic elements of report writing to graduate chemists. These people, supposedly trained in the basic principles of chemistry, could not even write a presentable informal report of their laboratory experiments. In fact, many of them could not so much as keep a decent daily log of laboratory procedure and results. What a reflection that is on their teachers and on their schools!

Most colleges and universities require no training in technical writing for chemistry students. Some of them require that once during the student's junior or senior year, a term report be sent to the English department for review. It should be noted that few teachers of English are trained to judge the validity of conclusions, the best manner of presenting data, graphing practices, proper statement of problem, items essential to a good discussion, and methods of presenting references. If the student's writing abilities are so bad as to appear almost hopeless, he may be assigned to a composition course—not, mind you, to a course in technical report writing, but reassignment to a type of course he once passed as a freshman. Is that logical? This type of haphazard arrangement, if in fact any arrangement at all has been made, is partly responsible for the poor quality of technical report writing.

Why should any self-respecting chemist allow such conditions and practices to exist? Even though he cannot, and probably should not, tack on fancy flourishes, can he not take enough pride in his article or book to make it accurate enough to assure other men that they can take his word? When the chemist is in his laboratory isolating his pet compound by his pet means, no care is too scrupulous, no method of insuring greatest accuracy is overlooked. It is *his* work, *his* pride, *his* joy. Why, oh, why is not his write-up of this experimental procedure an integral part of this *same* work, this *same* pride, this *same* joy? In reality his contem-

(*Continued on page 415*)

Peace Demands for Aluminum Expand

DAISY L. SCHOOLEY

Department of Commerce, Washington, D. C.

ALUMINUM—which went to war in a big way, from planes and ships to the G. I. mess kit—is now available to the manufacturer of civilian goods in greater quantities than ever before. Its lightness, strength, corrosion resistance, and dimensional stability make it particularly adaptable for use in many industries and products. From now on this versatile metal may be expected to become a part of our everyday life in increasing volume. From 1500 actual uses before the war, it has grown to around 3500, according to the results of a survey conducted by one of the basic aluminum producers.

Developments in processes, fabricating techniques, new alloys, and the creation of new uses made under war pressure, as well as the almost fantastic growth of the basic aluminum industry during World War II, are largely responsible for the public's light-metal consciousness. The knowledge acquired by the hundreds of thousands of people whose work brought them in close contact with aluminum will have a far-reaching influence on its future use.

Aluminum came into common use only about 58 years ago, and that is a brief span in a metal's history. Iron and copper have served mankind for thousands of years, lead almost as long, and tin and zinc have been used for centuries. The metal was first isolated in 1825 by the Danish scientist Hans Christian Oersted, but it was not until the discovery of a process for its extraction by electrolysis in 1886, simultaneously and separately by the 22-year-old Charles Martin Hall, and a Frenchman, Paul Louis Heroult, that an aluminum industry came into being.

Aluminum alloys may be fabricated into practically all the forms and shapes, and by all the methods used on other metals. It is produced in a wide variety of specifications for definite uses, and specialty products may even be had in colors to add appeal to consumer goods.

The large tonnage of aluminum required for war purposes necessitated the virtual elimination of its use in the manufacture of automobles, trains, electrical conductors, bridge and building construction, household utensils and appliances, furniture, packaging, and other nonessential civilian applications. The pent-up needs in these and other industries will require large quantities of aluminum during the next few years.

The accompanying table indicates the consumption of aluminum, as percentages of total use, by industries during the years just prior to our entry into World War II, and an estimate of early postwar uses.

CONSUMPTION OF ALUMINUM

Percentage of total use

Industry	*November, 1939*	*1940*	*1941*	*Estimate for postwar*
Transportation (land, air, water)	29	40	63	34
Cooking utensils	14	6	1	10
Electrical conductors	10	5	*	8
Machinery and electrical appliances	15	9	6	12
Building construction	8	5	3	9
Chemicals	5	5	5	5
Foundry and metalworking	4	23	19	9
Ferrous and nonferrous metallurgy	5	4	2	4
Food and beverage	6	2	*	5
Miscellaneous	4	1	1	4

* If any, included with miscellaneous.

Source: Bureau of Mines, U. S. Department of the Interior, for 1940–41 statistics.

Transportation—air, land, and water—is aluminum's biggest customer. This industry is expected to use at least one-third of the total consumption of the metal. The beginning of aluminum's success in the transportation field dates back to the built-for-two bicycles of the gay nineties, as some of these vehicles were equipped with rims, mudguards, and gear cases of aluminum. But it was in the aviation field that aluminum began really to rank as a major metal, and aviation, where lightness, not cost, has been the paramount consideration, has long been primarily aluminum's market.

An airline executive is credited with the statement that "every pound saved on a commercial plane is worth a thousand dollars." The importance of aluminum in aircraft is well demonstrated by the fact that, during 1944 alone, 96,369 airplanes of all types were delivered to the armed forces, with an average total weight of 10,600 pounds per plane, of which aluminum and its alloys are estimated to have accounted for at least 50 per cent. More than 50,000 pounds of aluminum went into the construction of every B-29 Superfortress.

While a considerable tonnage of aluminum will continue to go into plane construction—military, commercial, and private—the total annual consumption for many years to come is expected to be but a mere shadow of the wartime use.

Although the consumption in aircraft has dropped, greatly expanded use in bus, truck, and railway equipment is fast becoming a reality. The current trend toward light weight and high speed in commercial surface transport places aluminum in a very favorable position. In this field steel and iron are aluminum's primary competitors. On a weight basis, one pound of aluminum has the volume of about three pounds of steel; however, in the finished product the ratio may more nearly equal one to two, especially in parts bearing structural loads. By the use of the light metal it is possible to increase the payload materially and still observe highway regulations.

Inasmuch as the economies involved in operating a commercial vehicle are generally the determining factors, the decision rests on whether the somewhat higher initial cost of an aluminum unit is counterbalanced by that unit's lower operating cost. In addition to the pay-load factor, the lighter unit costs less to operate in terms of maintenance, fuel, oil, and tires and, in many instances, registration fees and taxes. In road transportation—bus, truck, or rail—the aluminum unit is carried on a steel chassis.

Bus lines are using increasing amounts of aluminum. For example, one of the country's large bus lines has for years employed considerable quantities of aluminum in its streamlined equipment. Government restrictions placed on the use of the metal during the war necessitated a switch-over to other materials, but the company's new equipment will reflect a reversion to the light metal. This company has on order several hundred of the "silver-side" type buses, each containing slightly more than three and one-half tons of aluminum. And a large manufacturer of motor-transport equipment is reportedly using considerable quantities of the metal in its newly designed, ultramodern line of motorbuses and trolley coaches which are to be used principally in interurban service.

The use of aluminum in trucks, trailer-trucks, and tank trucks is no novelty. Again, this is a field in which the pay load may be the determining factor in the increased use of aluminum. It is interesting to note that the quantity of aluminum that went into truck bodies in 1939 was twice that of 1938.

One of the producers of basic aluminum and its alloys announced recently that, through the cooperation of a large eastern urban trucking firm, its 16-foot-long aluminum trailer-truck would soon begin its road test. This trailer-truck is reported to effect a saving in weight of about 40 per cent over that of the conventional body now in use. An innovation in this line is the light-housekeeping trailer now being produced by a Chicago concern. A recent order by a United States Government Department for 400 of these trailers has been reported. The aluminum semitrailer refrigerator truck, developed during the war, was used by the Army in shipping perishable foodstuffs.

The passenger-car picture differs somewhat from that of the commercial vehicle. The 1946, and possibly the 1947, cars are not expected to show a material increase in the use of aluminum as most of them will be patterned after the 1942 models; however, by the time the new models roll off the assembly lines a definite upswing in the utilization of the metal is expected.

As in the years prior to World War II, most of the 1946 cars will have aluminum alloy pistons and rings. One of the big three in automobile production advertises that, in addition to these, its car will carry connecting rods, wire crimp in air cleaners, and oil-breather caps of aluminum, while a manufacturer of a midget car boasts a change-over to an aluminum body, crankcase, and camshaft bearings. A car of new design, made primarily of aluminum, was recently announced—production to begin six months after occupancy of the plant, for which negotiations are now under way.

An ultimate goal of 500 pounds of aluminum per passenger car is often cited. Such a figure may seem fantastic at present, but a gradual build-up to an average in that general neighborhood in the not-too-dim future is claimed as a possibility by some in the industry.

One aluminum producer claims that experiments made just prior to the war indicate that car doors made of aluminum stay in alignment longer and are easier to operate, and that the complete door with hardware weighs only 65 pounds, or 35 pounds less than a similar product of steel. The trunk door and hood could likewise be stamped from aluminum.

The producer further claims that the weight of a standard 3400-pound car could be reduced to 2300 pounds through the use of 500 pounds of aluminum in the engine and body parts and the redesigning of other structural parts made possible by this weight reduction. Such a saving would tend to offset the present price differential in the metals. A member of an industry research laboratory asserted recently that about 160 pounds of aluminum are required to aluminize completely the power unit of a 3200-pound, 6-cylinder automobile. Secondary aluminum is satisfactory for use in power units.

The industry expects the Nation's railroads to absorb large quantities of aluminum in the near future. The commercial use of the metal in this type of equipment began in 1923 when 25 urban cars were built with aluminum applications. The railroad company which constructed these supplemented its rolling stock with some aluminum equipment, as did a few others. In 1933 the first aluminum passenger coach and Pullman car were put on the rails, and in 1934, the first "all-aluminum" train. The all-aluminum train is carried on a steel chassis.

About the same time, the aluminum hopper car was given its experimental test by another railway. As aluminum is not affected by sulfurous materials, the aluminum hopper car is ideally suited for the transport of both soft coal and sulfur. One aluminum-ore producer uses such cars in transporting its bauxite. By the end of 1941 there was a noticeable trend toward the use of the lighter rolling equipment, although the number of aluminum units was small compared with the total in use.

The war temporarily suspended activity along this line, but interest in the lighter equipment is being renewed, as evidenced by recent developments. The few examples that are cited here give but a partial picture of the growing trend. At the close of 1945 orders were booked by six of the country's railroads for a total of 233 cars with all-aluminum superstructures, while 76 locomotives, each averaging about five tons of aluminum, are on order by two eastern railroads. The car orders include dormitory, standard and de luxe coaches; tavern lounge, grill, snack bar, and diners; parlor observation, and Pullman; baggage and mail cars. In addition, 10 double-decker, all-aluminum suburban coaches are on order by one line.

The first experimental boxcar with all-aluminum exterior began to roll last November. The use of 3722 pounds of aluminum in this 43,500-pound car effects a saving of 4057 pounds in total weight. The value of the aluminum tank car for the transportation of petroleum products and certain chemicals is well known. Skips with extensive aluminum application are used by some mining companies to transport tonnages on their own properties.

Aluminum will continue to go to sea but, as in the case of aircraft, the quantity involved in peacetime application, though sizable, will be small as compared with its war use. Some idea of the wartime requirements is indicated by the amounts of the metal that go into individual types of naval units. An aircraft carrier consumes 2,000,000 pounds of aluminum in its construction; a battleship 1,400,000 pounds; a heavy cruiser, 600,000 pounds; a light cruiser, 500,000 pounds; a destroyer, 225,000 pounds; a large auxiliary ship, 60,000 pounds; a small auxiliary ship, 20,000 pounds; and a submarine, 15,000 pounds.

The wide use of aluminum in wartime vessels may set the pattern for increased utilization of the metal in commercial seagoing craft. Many postwar merchant and passenger ships will include aluminum in their superstructures, bulkheads, stacks, masts, hatch covers, air ports and windows, passenger stairways, ladders, railings, and furnishings. In addition to new construction and repair of the larger craft, applications will include outboard motors, lifeboats, small boats, canoes, and rafts. A large producer of airplanes has already added aluminum canoes to its line.

Vertical transport is not to be overlooked in the field of conveyance—freight and passenger elevators may well employ the light metal in larger quantities to gain greater lifting speed, save power, and lengthen the lift of component parts.

Construction, also, is considered by aluminum producers as a fertile field for the use of their products. Aluminum enters construction—commercial and private, nonresidential and residential—in many forms and finishes. Its more general applications include window frames and sashes, door frames and doors, balustrades, marquees, spandrels, grilles, trim, screens, elevator enclosures, hardware, store fronts, and insulation. The design of the grille and spandrel is limited only by the designer's imagination in using the bright metal to create patterns of beauty.

The 100-ounce cast cap of aluminum placed on the peak of the Washington Monument in the Nation's capital in 1884, when the metal was still in the precious-stage category, is one of its earliest uses for architectural or building purposes. It was not many years after the commercial production of aluminum became feasible (1886), however, that it made its appearance in building construction. In fact, a number of outstanding structures of the nineties had some aluminum applications.

An example of the adaptability of aluminum to modern architecture is its use, to the extent of about 226 tons, in the United States Department of Justice building in the District of Columbia. Other prominent buildings that contain large quantities of the metal include the Empire State Building, New York City, with its aluminum spandrels, store fronts, and mooring mast; the buildings of the Rockefeller Center Development, New York City, with aluminum spandrels, window frames and sashes, and ornamental trim; the Marshall Field Building, Chicago, with aluminum spandrels and window frames and sashes; and the Cincinnati Union Terminal, in which all of the interior metalwork is of aluminum—nearly 43 tons of aluminum went into a new roof for the terminal recently.

The use of aluminum roofing is no innovation, but its employment in low-cost buildings is a new development. The present shortage of other roofing materials is reflected in the orders placed by jobbers and dealers in farm supplies throughout the United States for millions of pounds of corrugated and batten-type aluminum roofing.

Many of the forthcoming prefabricated homes will use aluminum extensively, as well as steel and plastics. A radically new type of building for mass factory production is scheduled to have both outer and inner walls of aluminum sheet with aluminum insulation, and possibly other aluminum features. A producer of basic aluminum is planning a complete bathroom unit of aluminum for use in rural homes.

In the past, large quantities of aluminum foil have been used as wrappings, for decorative labels, and for insulation. As a wrapping, it is widely used on candy, tobacco, chewing gum, ribbons for typewriters and other business machines, friction tape, photographic films, and similar products. New ideas in developing protective wrappings and containers for the Army will have

postwar applications. For instance, aluminum caps and seals made for penicillin bottles will have peacetime counterparts in packages designed for pharmaceuticals, while heat-sealed, aluminum-foil envelopes such as were used during the war will protect some of the dehydrated soups and powdered fruit juices.

A household foil, which can be torn from the original package in suitable-sized pieces, is expected to reappear upon the market shortly. It can be pressed on bowl tops or around food products, and may be used and reused many times. This type of foil is said to have been used recently by a home-gardener in forcing the germination of vegetable seeds.

The reflective property of aluminum has resulted in the foil's being employed extensively for insulation. Aluminum-foil insulation was used by Admiral Byrd in his Antarctic home for added protection against abnormal temperatures. In anticipation of the greatly increased postwar market for aluminum foil, two large producers recently announced their intention of materially expanding their production facilities.

Aluminum paint is another product that is growing in popularity. The desirable properties of the paint—resistance to heat and cold, prevention of bleeding, heat reflectivity, and hiding power—have firmly established it in many industrial fields. For instance, aluminum paint assumes a degree almost of essentiality for covering oil-storage tanks in tropical areas to minimize evaporation. The paint reflects a large amount of the light and radiant heat falling on its surface.

Aluminum's nontoxic and noncorrosive properties have resulted in its steadily widening sphere of usefulness in the dairy, brewery, and chemical industries. Besides these, other industries employed large tonnages of aluminum in the prewar period, and it is likely they will continue to do so. The metal's high electrical conductivity extends its use to conductors in central stations, as well as for high-tension transmission and rural distribution lines. It is used in the oil industry, particularly, as previously stated, for storage purposes, and is employed in steel production where it is used to deoxidize and purify the molten metal. Steel's 1945 production of almost 80 million tons required roughly 40 thousand tons of aluminum; secondary aluminum satisfies the major part of this use.

Large tonnages of aluminum also annually enter into the production of many articles of everyday use, including radio apparatus, electrical equipment and appliances, refrigerators and parts, vacuum cleaners, cooking utensils, meters and gages (both gas and water), refrigerators, ice-making, humidifying, and air-conditioning machinery, high-speed machine parts, washing machines, gas and electrical fixtures, including lamps and reflectors, office equipment, such as adding and calculating machines, cash registers, typewriters, and check writers, food-processing equipment, and bottle caps and enclosures. Because of the metal's resistance to corrosion, the aluminum industry expects the rayon, sugar, explosives, and rubber industries to increase their consumption.

Aluminum shows up often in new kitchen, porch, lawn, and garden equipment. Easy-to-handle aluminum products, such as tools, chairs, tables, stepladders, wheelbarrows, and lawnmowers, are a few of the many interesting items.

One of the new applications of the metal is in the handie-talkie—a commercial counterpart of the small military radio and largely a development of war research and experimentation—which will soon be available for public use. This piece of equipment owes its lightness (five and one-half pounds) to the extensive use of aluminum.

A manufacturer of the spinet-type piano uses an aluminum plate for the strings; since the plate weighs only 45 pounds, a saving is effected of about 90 pounds over the material formerly used. A large manufacturer of keys and locks is claimed to have used recently a sizable volume of the metal for keys. Artistically designed name plates or markers for country homes or estates are now being cast from aluminum. Another new development is aluminum thread, a by-product of foil production; one pound of aluminum is thus stretched nearly six miles.

Paradoxical as it may seem, the increased use of aluminum in certain lines may well serve to stimulate the consumption of the materials which it seems to have displaced. Many industrialists feel that the substitution of aluminum in certain durable goods, such as transportation equipment, may be expected to continue to increase, but that the further use of metals and other materials affected by such substitution will not be retarded. They reason that the product improvement and operation economies brought about through the wider use of aluminum will cause a greater economic demand for the materials it supplements.

ALUMINUM PRODUCTION

(In thousands of pounds)

Year	Primary	Secondary		Total
		From new scrap	From old scrap	
1939	327,090	32,368	75,526	107,894
1940	412,560	69,112	91,612	160,724
1941	618,134	127,488	86,226	213,714
1942	1,042,212	309,662	83,266	392,928
1943	1,840,358	561,734	66,188	627,922
1944	1,552,892	605,492	45,798	651,290
1945*	1,050,000	†	†	610,000

* Estimates.
† Not separately estimated.
Source: Minerals Yearbooks, Bureau of Mines, U. S. Department of the Interior, for 1939–40 statistics.

Since aluminum was last available for civilian use, competition has entered the field of basic aluminum production. Two producers are now operating in this field and two others are negotiating for the use of government-owned aluminum facilities. Adequate capacity for and competition in the production of basic aluminum should create new and expanding patterns of aluminum use.

The aluminum industry is looking to the engineers who design our machines for industrial use and our products that make for better living to utilize aluminum as one of their important components.—Reprinted from *Domestic Commerce* (April, 1946).

THE EDITORIAL OFFICE MOVES

On or about September 1 the editorial office will be moved from Brown University to the

Scripps Institution
La Jolla, California

Thereafter, all mail intended for the Editor should be directed to the latter address.

The Semimicro Detection of Thiocyanate and Halide Ions

LYMAN E. PORTER

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THE detection of the halides in the silver nitrate group is complicated by the presence of the cyanogen anions and sulfide. The ferrocyanide, ferricyanide, and sulfide ions may be removed before the use of the silver nitrate by means of a zinc salt[1, 2] or a cadmium salt.[3, 4] If we leave out of consideration the cyanide ion, which is better omitted from unknowns for student use on account of its extremely poisonous character, only the thiocyanate and the halides are left to be precipitated by silver nitrate in the presence of nitric acid. The removal of the thiocyanate before the detection of bromide seems to be of unusual difficulty in the hands of a class. An excellent summary of the literature concerning this separation is given by Hart and Meyrowitz.[5] The use of ammonium sulfide for the removal of the silver presents some difficulties, resulting too frequently in the loss of bromide. The decomposition of the thiocyanate by warm nitric acid results in too many cases in the oxidation of all of the bromide.

The following method has been developed in this laboratory and has been used with several classes in second-year chemistry with satisfactory results. The separation of the thiocyanate from the bromide depends upon the formation of its complex ion with ferric ion (probably $FeSCN^{++}$) when the precipitated AgSCN is suspended in a solution of hydrochloric acid and treated with ferric chloride. The bromide is not changed in this process. The probable course of the reaction is given by the equation,

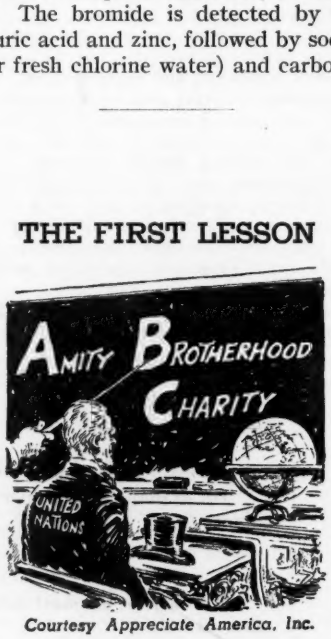
$$\underline{AgSCN} + Fe^{+++} + Cl^- = FeSCN^{++} + \underline{AgCl}$$

This is a similar reaction to those for the decomposition of AgSCN by hot sodium chloride solution[6] and by potassium bromide,[4] but it proceeds more easily due to the formation of the complex ion. The separation and the detection of the thiocyanate are done at the same time, making it easy to tell when the removal has been complete and assuring better results in the subsequent test for bromide. From the teaching standpoint the equilibrium relationships that are involved give an opportunity for some worth-while class discussion involving solubility products and an instability constant.

PROCEDURE

To the solution from which ferrocyanide, ferricyanide, and sulfide ions have been removed as the zinc or cadmium salts, nitric acid is added to distinct acidity, followed by silver nitrate until precipitation is complete. After centrifuging and washing, part of the silver chloride is dissolved by the use of 1 ml. of 3 molar ammonium carbonate, and the chloride detected by the addition of an excess of dilute nitric acid. The residue from the carbonate treatment may contain AgSCN, AgBr, AgI, and some AgCl. This is treated with 7.5 molar ammonia to dissolve all but the iodide. The iodide is detected by treatment with dilute sulfuric acid and zinc metal, and the resulting solution, after separation of the excess of zinc and the silver, is treated with potassium nitrite and carbon disulfide. The ammoniacal solution from the iodide separation is acidified with dilute nitric acid and the precipitate centrifuged and washed. This may consist of AgSCN, AgBr, and some AgCl. The residue is then treated with 1 ml. of water, 5 drops of 6 molar HCl, and 5 drops of 2 molar $FeCl_3$. The mixture is stirred thoroughly. The formation of a red or reddish brown solution shows the presence of thiocyanate. Centrifuge after three or four minutes, and repeat the treatment with HCl and $FeCl_3$ until no more $FeSCN^{++}$ color is produced. One repetition is usually sufficient. The residue is washed with water containing a few drops of dilute nitric acid to remove ferric ion. The bromide is detected by the use of dilute sulfuric acid and zinc, followed by sodium hypochlorite (or fresh chlorine water) and carbon disulfide.

THE FIRST LESSON



Courtesy Appreciate America, Inc.

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A Simple Sublimation Apparatus[1]

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PRELIMINARY purification of substances by sublimation is frequently desirable, but apparatus usually described for this procedure offers difficulties in the handling of the sublimate. The laboratory apparatus described below has been used with success for the purification of a number of compounds. It possesses the advantages of simple construction, ease of operation, rather wide adaptability. The sublimate is reasonably pure and is obtained in good yield.

The apparatus shown in the diagram consists of a four-foot length of pyrex tubing, *A*, 55 mm. O. D., fire-polished on both ends. The tube *B*, in which the charge is placed, is made from 45-mm. O. D. pyrex tubing drawn to a diameter of about 20 mm. at one end and tooled for a No. 8 rubber stopper at the other. The over-all length of this tube is about two feet. The collecting tube, *C*, consists of a piece of pyrex tubing, 45 mm. O. D., about 20 inches long, to which has been sealed a 12-inch length of 20-mm. tubing. The large opening end of this tube is fire-polished. An electric furnace wound on an 18-inch length of two and one-half inch leader pipe and covered with asbestos and rock wool insulation serves as a furnace, *D*, for the sublimation. The furnace is so constructed that the desired range of temperatures can be covered by regulation with a variable transformer.

The outer tube is placed in the furnace and brought to the desired temperature. The material, *F*, to be sublimed is placed in tube *B* with glass wool plugs, *E*, to prevent spreading of the powder. A one-hole rubber stopper, fitted with a gas delivery tube which also carries another rubber stopper, holds the charge tube in place.

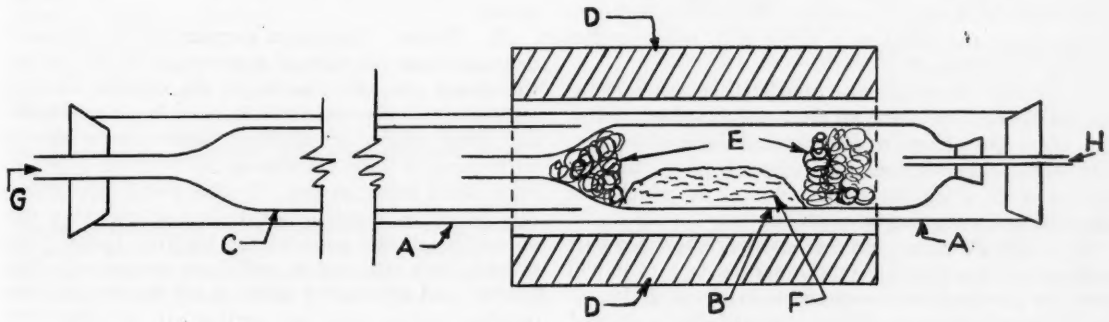
Before the charge tube is placed in position, the collecting tube, *C*, is introduced, fastened with a rubber stopper between the outer tube and the small diameter exit end, and then connected with rubber tubing to a suction line or to a water aspirator. The loaded charge tube is now placed in position so that it butts against the collecting tube. Any gases that are to be passed through the tubes during the sublimation are introduced through *H*.

We have used this apparatus for the successful purification of substances such as selenium dioxide, arsenious oxide, and phosphorus pentoxide. In all of these cases the products were of high purity and were obtained in good yield.

For example, a charge of 350 grams of selenium dioxide can be sublimed completely in 90 minutes; and if care is taken to perform this operation in a stream of oxygen to which a small amount of nitrogen dioxide is added, the product is obtained in white acicular crystals which hang from the wall of the tube. This material can be removed by scraping. If a solution is required, the tube *C* is placed vertically in water which is then drawn into the tube by suction applied at *G*.

The materials of construction in the apparatus described do not permit operation above temperatures of 480°C. A similar apparatus, however, can be constructed of vycor or quartz.

The author wishes to acknowledge the suggestions and the assistance of Mr. William Primak in the construction of the apparatus.



[1] This paper is based on work done for the Office of Scientific Research and Development under Contract Number OEMsr 982 with the Polytechnic Institute of Brooklyn.

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Crystallization

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WHEN a dilute solution is allowed to evaporate spontaneously, a point is presently reached at which the solvent is saturated with the solute. At that point crystallization begins and continues until the solvent is completely removed. Interesting and beautiful results may be obtained in the experiments that follow.

1. General Results. Prepare dilute solutions of potassium sulfate, potassium hydrogen sulfate, sodium chloride, lead nitrate, potassium chromate, and other salts. Filter (if necessary) into crystallizing dishes and let stand until the solvent has completely evaporated. Some solutes may develop the creeping effect; a little vaseline rubbed around the upper inside rim of the dish will prevent this. K_2SO_4 gives hard, glassy, diamond-shaped crystals; $KHSO_4$ yields long white needles; NaCl produces white cubes with a dark spot (water) in the center of each; $Pb(NO_3)_2$ gives shapes resembling an equiangular triangle with the vertices cut off on a line at right angles to the bisector of the angle, the sides being alternately long and short. Others will, of course, yield varying shapes.

2. Crystallization on a Form. Procure some pipe cleaners and cut two of them in halves. Using ordinary sewing thread, tie four ends firmly together, leaving a long thread to be used later. Soak in water. Remove and bend the free ends outward and downward. Suspend this form in a hot saturated solution of potassium dichromate to which potassium sulfate has been added. Support the form by means of the thread to a support above. When the solution is cold, remove the form; it will be covered with fine red crystals of the dichromate with white crystals of the sulfate here and there, giving the effect of a shrub with red branches bearing white flowers.

3. Copper Formate. Stir powdered copper carbonate into formic acid until no more will dissolve. Filter and allow the filtrate to evaporate. Cubic blue crystals form. Since these are hydrated, they may be preserved in a tightly stoppered vial to which one small drop of water has been added.

4. Cobalt Formate. Proceed as above, using cobalt carbonate. The dry crystals preserved in a tube will glow like live coals when exposed to bright sunlight.

5. Sugar Crystals in Jellies. Beautiful crystals may often be noted in glass jars containing jams, jellies, preserved fruits, etc.

6. Purple Chrome Alum. Stir powdered potassium dichromate into 25 cc. of dilute sulfuric acid in a beaker until the action is complete. Stand the beaker in a cooling mixture and stir in alcohol, using a thermometer, a little at a time; the odor of formaldehyde will be noted. Keep the temperature below 30°C. When action is complete, let stand. Eventually beautiful purple crystals of chrome alum will form. Let the sunlight shine through some of them.

7. Ammonium Oxalate. To a hot solution of oxalic acid add ammonium hydroxide until the whole is neutral. When cold, the beaker will contain white needles of ammonium oxalate.

8. Lead Iodide Spangles. Fill a 50-cc. graduated cylinder with hot water to warm it. In a beaker add a gram or two of powdered lead iodide to 50 cc. of water near the boiling point. Pour the contents of the cylinder into a filter to warm it. Discard this liquid and pour the contents of the beaker into the filter, catching the filtrate in the warmed cylinder. As the hot liquid cools, brilliant spangles of lead iodide form.

9. Projecting Crystal Growth. Lay a clean glass plate across the ring of a stand or a tripod. On the center of the glass place a drop of saturated barium chloride solution. An electric lamp below will warm the glass so crystallization will soon begin. A magnifying mirror may be so placed as to project the process onto a screen where the crystallization may be observed by a class. Using another glass, other saturated solutions may be used and the differences in crystal forms noted.

10. Sulfur. The size of a crystal obtained as above depends upon the rate of evaporation of the solvent; the slower the rate, the larger the crystal. Dissolve a gram or two of powdered roll sulfur in carbon disulfide and filter into a crystallizing dish. Cover the dish with three or four thicknesses of blotting paper and lay a wood block on top. In this way evaporation of the solvent is much delayed since it can take place only through the pores of the blotting paper. After several days the solvent will have completely disappeared, and crystals of sulfur much larger than those obtained by the usual evaporation will be found.

Reactions from Our Readers

The following comments, offered by a few of our readers in response to the editorial questionnaire of some time ago, are quoted not to justify present policies or to pat ourselves on the back, but because they contain points of intrinsic interest which we think other readers will recognize.

My experience with chemistry teachers indicates that they feel the JOURNAL is not adequate to their needs for these reasons:

1. Too advanced.
2. Not enough helps on the high-school level.
3. Needs more content of all kinds, advertising, equipment, theory, and present-day practices.

This situation is not due entirely to the editorial policy but chiefly to these factors, I think:

1. Divided interest of chemistry teachers to physics, botany, etc.
2. Failure of those of us that enjoy and use the JOURNAL to sell it to others.
3. Economic situation of many high-school teachers.

I believe the JOURNAL should make a definite effort along the line of vocational guidance. The American Chemical Society, through the local sections and the *News Edition*, has proved invaluable to its younger members; however, it does not adequately reach the students who are making their final decision as to course of study and life work.

The only picture most students have is the beautiful, well-equipped college laboratories and the mystic haze cast about chemists by popular conception and fantastic movies. If the student were made fully aware of his responsibility and at least partially understood the problems before him I believe he would work with increased diligence and be a much greater force in the interest of the profession.

Chemical education is not only the education of the high-school or college scholar but of the adult as well.

I would like to see published a possible curriculum to be set up for the training of nonlaboratory workers. Many good men are lost to the chemical industry each year because our schools fail to impress certain good students with the advantages of non-laboratory positions in chemistry.

We work hard trying to give our private-school students an edge. Couldn't we have a series of articles or a committee to investigate and tell us, in the secondary school, what the colleges want their students to know? Is it more mathematics, more chemistry, more theory? What shall we devote our energies toward?

Departments of education have put chemistry into high-school curricula, selected teachers regardless of their qualifications to teach chemistry, and turned them loose. College chemistry departments have ignored the work done by the high school or condemned it.

As long as it seems that chemistry is going to be offered in high schools, couldn't some way be worked out to prepare the teachers or set up standards for them that would prove of value both to the high school and the college?

As a rule only technical high schools in the largest cities have chemists as teachers, and so the smaller high schools are at a disadvantage. Couldn't the JOURNAL sponsor a movement to get the college chemistry departments, the education departments, and the high schools together to the advantage of all concerned? Could, or should, more chemistry students in college be steered into the *teaching* of chemistry—not let the teacher be merely anyone who happened to have a course in general chemistry?

(The following, from a student, reveals a curious train of thought.)

New theories (advanced, as usual), especially those showing weak spots in other theories (the ones we're trying to learn), would only cause confusion if they were read. It is difficult enough to master what we are being taught; therefore, the JOURNAL should supplement, not supplant.

The quality of your contributors might be improved. A few, but not enough, men of high authority in the profession bring their wisdom to the JOURNAL and thereby to the world's new generation. Yours is an important journal and should be dealt with in an important way, not by cold amateurish monographs which cannot reach print otherwise, but by enthusiastic and scientifically distributed attacks on the problems of teachers in making chemistry live and grow for the pupil.

The JOURNAL in its present form means almost nothing to me. I look it over for N.E.A.C.T. news and the one article of interest to high-school teachers and new books. I have been told this same thing from many high-schools teachers. I judge most of the subscribers are high-school teachers [about 25 per cent—Ed.]; if so, why so much college "stuff?" We high-school teachers want some help to help us to teach better.

I have heard high-school teachers say that the JOURNAL is too advanced for their students. Personally, I do not think the JOURNAL is destined for their students' consumption but for the teachers' digestion. . . . I believe that in receiving the JOURNAL every month I receive an "up-to-the-minute" source of current chemical theory and industrial progress, as well as suggestions from other teachers. I consider it good professional conduct for the teacher of chemistry to want the JOURNAL to be just that. From that point on, the teacher will bring down to his students' level what he deems necessary to keep them well informed. (*By a high-school teacher.*)

(The following were among the suggestions for new or additional features):

Fewer articles such as Vol. **22**, No. 9, September, 1945, page 418. ("Wave mechanical considerations.")

Continuation of articles such as the ones on wave mechanics.

A few more topics that would be of interest to high-school students, similar to the one on "Batteries" in Vol. **22**, page 485.

I do not believe that in view of the number of students served directly compared to teachers and others served, such recent popularizations as the one on batteries in the August issue are worth the space taken. They introduce no new ideas, no teaching points, are too elementary, and even for students are rather silly.

Better written and more interesting articles. (Authors, please take notice—Ed.)

Out of the Editor's Basket

Although there is supposed to be a general impression to the contrary, college students like their teachers—even in engineering schools where the work is heavy. Rensselaer Polytechnic Institute came to the conclusion after polling an anonymous cross section of students from all 12 departments at the science and engineering school.

"Are student-faculty relationships satisfactory?" asked the Institute. Seventy-four per cent of the students said they were. Only 26 per cent disagreed, although they have had to forego such pleasures as the traditional summer vacation because of war-impelled study accelerations.

The students were asked to rate, in order of importance, the factors contributing to their estimate of a professor. Most important, said the students, is his personality and manner in the classroom. The second most important factor is how fair he is in grading. Next, the books and articles he writes, his degrees, and in last place, his official rank in his department.

Ninety-four per cent of the students voted that campus forums for discussion of international and national issues are important. Eighty-three per cent voted that debating contests with other colleges are important.

The students listed many factors as contributing, in their opinion, to "produce a favorable general reputation for a science and engineering school," but the principal items were ability and success of graduates, reputation and experience of teachers, and research facilities and achievements, in that order.

Asked their preference on teaching methods, 61 per cent favored the discussion method, 19 per cent the lecture method, while 10 per cent preferred a combination of the two, and 10 per cent were noncommittal.

Sulfuric Acid

A map has been published by the U.S. Department of Commerce showing the geographical location of sulfuric acid plants throughout the country (13 states have no plants within their borders). There is also other information on the production and consumption of H_2SO_4. It is in the June 5 issue of *Facts for Industry*, published by the Bureau of the Census.

Condensers

A new German method of making paper-fixed condensers is to "vaporize" a thin deposit of zinc directly on the paper dielectric. Voltages 20 to 50 per cent higher are claimed to be withstood, compared with the older metal-foil type of construction.

New Titles

In establishing certain new positions within its organization, the Calco Chemical Division of the American Cyanamid Company has borrowed titles from the academic field and given them an industrial significance of high standard.

The first is the position of Research Associate, "to recognize high scientific attainments and wide experience in both the prosecution and direction of the research of the Company. Research Associates are relieved of the responsibilities for detailed administration of a regular unit of research in order to be available for important special assignments in the Research Department. They must have had not less than 20 years of professional experience since receiving the Doctor of Philosophy degee or its equivalent and must have been in the employ of the Company not less than ten years, five of which were spent in directing or supervising the research work of others. The position is comparable with an executive position in research requiring similar experience and entailing equivalent responsibilities."

The second position, at a slightly lower level, is that of Research Fellow, "to recognize outstanding ability for individual research. The position affords the opportunity for properly qualified scientific personnel to concentrate on research without the handicaps imposed by supervisory responsibilities. Research Fellows must have had not less than ten years of professional experience since receiving the Doctor of Philosphy degree or 15 years of professional experience since obtaining the Bachelor's degree, and must have completed five years of continuous service in research with the Company. The position is comparable with a supervisory position in research requiring similar experience and attainments."

German Patents

Ten tons of documents taken from the German Patent Office are now being sorted and evaluated and will eventually be disseminated for the benefit of American science and industry. Originally seized by the United States Army in Germany, the documents were shipped to Wright Field in 146 packing cases. Army authorities then turned the documents over to the Office of the Publication Board, Department of Commerce, for dissemination to the public through its facilities. The United States Patent Office and OPB are cooperating in sorting and evaluating the documents.

Prior to 1939 patent information was regularly exchanged between Germany and this country. Since then, however, thousands of German patents have been issued of which we have no knowledge. It is this file of patents issued during the war that is of particular interest to the United States Patent Office, and many of these patents will be placed on file in the Patent Office Search Room for public use.

Polio

The polio virus can be inactivated by free chlorine residuals well within the range of practical dosages used in water treatment, according to G. M. Ridenour and R. S. Ingols of the University of Michigan School of Public Health. Furthermore, the effectiveness of the free chlorine residual is independent of the type of chlorine-bearing compound as long as the equivalent oxidation potential of free chlorine exits.

According to the investigators, previous investigation had led to the belief that the amount of chlorine and the time of contact required for disinfection against the polio virus were beyond practical limits, and therefore, if poliomyelitis were determined to be a water-borne disease, chlorine would not be practical for inactivation. They point out, however, that these investigations were based on the orthotolidine test for determining residual chlorine. This test measures not only uncombined chlorine, but also various chloro compounds which "by virtue of their lower redox potential have lesser disinfectant capacity" than "free" chlorine. The authors have used, instead, the recently developed orthotolidine-arsenite (OTA) test, which measures only "free" chlorine or its equivalent oxidation potential.

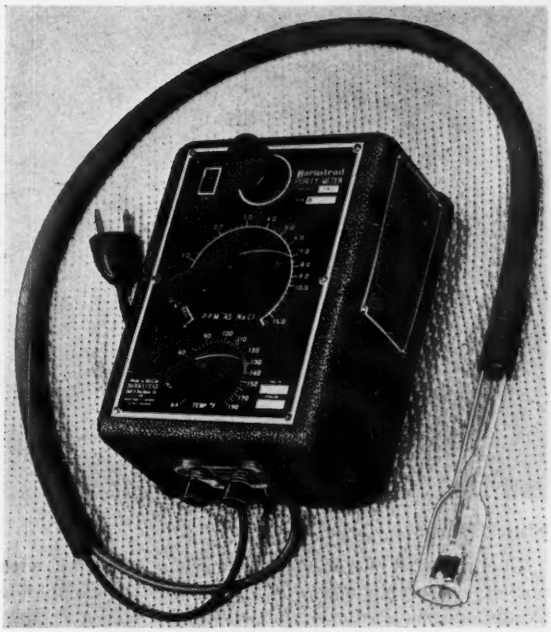
In conducting their research, the authors used water treated with chlorine or with chlorine dioxide generated from sodium chlorite. They found that the results were about the same for chlorine, chlorine dioxide, or a mixture of the two, provided sufficient "free" chlorine residual was supplied. "The results from these studies show that chlorine, now in universal use for disinfection of water, can be used in amounts which will result in inactivation of poliomyelitis virus and yet produce a satisfactory and palatable water."

In view of the marked difference in results obtained through the use of the new OTA test, the authors suggest that "methods now in operation for chlorination of community waters in general be reëxamined to determine their efficiency in providing free chlorine."

Synthetic Gasoline

Although proved reserves of petroleum in the United States are currently at the highest point in history, it is regarded as important to explore the possibilities offered by science to add to such reserves by synthetic fuels. These can be produced from abundant supplies of natural gas, coal, oil shale, and tar sands.

The Navy's Bureau of Ships recently asked for several barrels of synthetic gasoline and synthetic Diesel fuel, meeting Navy Specifications. The synthetic gasoline, for example, had to be of 80-octane rating, matching the all-purpose gasoline used by U. S. Army vehicles during the war. Working with natural gas, the Esso Laboratories produced both the synthetic gasoline and synthetic Diesel fuel by the hydrocarbon synthesis process —a further development of the basic fluid catalytic technique which enabled Jersey Standard to turn out sufficient 100-octane gasoline in wartime to power one out of every four U. S. and British warplanes.



Water Testing

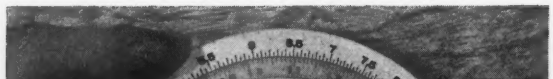
A new model of the Barnstead "Purity Meter" has appeared. The instrument measures conductivity, translated into parts per million of dissolved NaCl (representative of total solids).

Synthetic Caffeine

Monsanto Chemical Company has succeeded in synthesizing caffeine, and is erecting a $1,500,000 plant for the process at St. Louis. So far as we know this is the first instance where so complicated a molecule as caffeine (the molecular weight of which is 194) has been synthesized from its ultimate components, hydrogen from water and nitrogen from air. Simple products, such as methanol and formaldehyde, have been produced in this way, but synthesizing caffeine represents a much more important research achievement.

Science in South American Schools

Schools in South America sponsored by U. S. groups are not only doing an excellent job in interpreting our culture and ideals to our southern neighbors, but they are pioneering in the development of laboratory courses in science. They offer a real challenge to the science teacher in unlimited opportunities for service to the young Latin Americans who are avid to master the mysteries of science. Dr. Roy T. Davis, Director of the Inter-American Schools Service of the American Council on Education, Washington, D. C., reports that far more progress could be accomplished were it not for the lack of qualified teachers. He will be delighted to advise teachers who are interested in this field as to how to obtain positions. Candidates should not be deterred by a lack of knowledge of Spanish which, although desirable, is not absolutely necessary.



Slide Rule

The precision of a 12-inch slide rule is combined with pocket-size convenience in the simplified Calculaide Commerce slide rule developed by American Hydromath Company, New York. Only four and one-half inches in diameter, this new type of circular slide rule incorporates many advantages over both traditional slide rules and conventional circular slide rules.

Measuring Humidity

Two types of instruments for remote measurement of humidity at room temperatures and at subzero temperatures have been developed by the U. S. Army.

For measuring humidity at room temperatures, a thermoelectric psychrometer was developed. It consists of a pair of fine wire thermocouples, one of which is continuously wetted by a wick. The device permits remote reading of humidity without requiring forced air movement past the wet bulb, as do mercury-in-glass psychrometers. For this reason it is particularly useful for measuring relative humidity in small enclosed spaces, such as storage dumps, and in tests where no air disturbances are permitted.

The other instrument is an electronic dew point recorder, designed for the measurement of humidities at subzero temperatures. This recorder automatically adjusts the temperature of a small mirror exposed to the air so that it is continuously on the verge of being fogged. The mirror temperature (dew point) and the air temperature are recorded and can be translated into relative humidity. The temperature of the mirror is maintained by constant cooling with a refrigerant and through variable heating by a radio frequency induction heater. A photoelectric cell scans the mirror and automatically adjusts the temperature in such a manner as to prevent actual fogging.

Chemical Show

This year the National Chemical Show will be held in Chicago concurrently with the meeting of the American Chemical Society, from September 9 to 13.

Titanium

Extensive wartime research on titanium in Germany may offer unusual possibilities for the future use of this metal by the electrical, the machine tool, and other industries. The only German titanium manufacturing firm, Titangesellschaft, was investigated by Ford H. McBerty of the Technical Industrial Intelligence Branch, Department of Commerce.

According to reports, titanium may have extensive uses in the field of dielectrics and, in the carbide form, may become more than a mere substitute for other carbides in high-speed tools where minimum wear is required. The Germans used titanium compounds for coating welding rods, as a substitute for borax in the preparation of vitreous enamels, as a paint pigment, in the manufacture of paper and textiles, for dielectrics and partial electrical conductors, for cemented machine tool cutter tips, and as a fog (titanium tetrachloride) for screening troop movements.

Bleaching Fats

Crude fats normally used to make only the harsher laundry soaps are now being employed to make high-grade soaps and soap flakes as the result of a bleaching process developed by the Mathieson Alkali Works. The new process, which makes use of sodium chlorite, was developed as a result of the wartime shortage of fats and oils and has been used successfully on a commercial scale for about a year.

Heretofore, chemical methods have rarely been used for improving the color of fats because of the fear that the soap-making qualities of the fat might be unfavorably affected. With sodium chlorite bleaching, however, there is no chemical deterioration of the fat, and both color and odor are greatly improved. Moreover, the yield of tallow is considerably greater than when filtration and absorption methods of color removal are used.

Canned Bread

Canned bread, made in quantity for military purposes in Germany during the war, is said by the Germans to keep for as long as ten years, according to U. S. technical investigators. They report that the bread slices well, seems rather soggy and heavy, but has a good taste.

A German master baker states that the bread, called "Dauerbrot," may be made in any desired way and according to any desired formula. His own recipe called for 200 kilograms of rye flour mixed with 180 to 190 liters of water at 26°C. To 100 parts of this mixture he added 45 parts of a ferment dough. The entire mass was then kneaded, formed into dough balls by a rolling machine, and placed in special round or square tins. It was baked at 220–250°C. for 80 to 90 minutes.

Round pans were used for bread that was to be hermetically sealed in cans, sterilized, and stored indefinitely. Square loaves were wrapped and stored for two to three months.

Humidity in Photography

Humidity is the most important factor in dimension changes of photographic films and papers, according to an Air Technical Services Command memorandum report. It was found that both shrinkage and expansion result from differences between the humidity of the film and that of the surrounding atmosphere. As the film ages, irreversible shrinkage occurs because of loss of volatile solvents in the base. Tension on the film does not result in permanent deformation even though it amounts to several hundred pounds per square inch.

In mapping film total shrinkage is less important than the difference between crosswise and lengthwise shrinkage, according to the report. The difference may be offset by "crossing" negatives and papers in making prints, but this precludes the use of continuous printers.

For military mapping the laboratory recommends the use of acetate topographic film. This should be conditioned in an atmosphere of 65 per cent relative humidity before printing. Printing papers should be similarly conditioned if possible.

In processing, excessive heat and accelerators, such as alcohol and acetone, should be avoided; however, the use of wetting agents before drying is recommended to prevent water spotting and local movements of the silver image. Where greater accuracy is required than these methods permit, the laboratory recommends the use of glass plates and special paper of the aluminum sandwich type.

Egg Substitute

A synthetic substitute for egg white has been made from fish and used successfully for food and technical purposes in Germany since 1934, it is said. The product is claimed to have excellent food value and to have only a faintly perceptible fishy flavor. The synthetic material can be used in the same way as egg white and is said to have superior whipping qualities.

Fresh fillets of codfish are preferred for the production process, although dried codfish and steam-dried shrimp were also used. The process was developed at the plant of the Deutsche Eiweiss Gesellschaft in Wesermunde and involves removing readily soluble proteins with dilute acetic acid and extracting lipids with trichlorethylene. The extracted tissue then is stirred in warm dilute sodium hydroxide, and the partly hydrolyzed protein is neutralized with acetic acid and spray-dried into a white powder.

One analysis of the powder showed that it contained 93.9 per cent protein, 4.65 per cent water, varying percentages of salt, calcium oxide, total ash, lecithin phosphoric acids, and total phosphoric acid, 0.003 per cent of organically bound iodine, and a trace of fat.

Periodic Table

The periodic table, arranged by W. F. Luder and published in our January, 1943, issue, has been issued as a wall-chart by the W. M. Welch Manufacturing Company.

Dressed to Kill

Knights in olden days used to wear steel armor when they sallied into battle, and today's fine lady also wears steel when "dressed to kill"—but in the form of smart new jewelry made of stainless steel. Everything from headbands to shoe buckles in lustrous stainless steel was recently on display at the National Metal Exposition in Cleveland.

The jewelry, which was fashioned by A. D. Celapino of Belle Vernon, Pennsylvania, is of fairly intricate design—much of it made from stainless steel wire twisted and braided. Included in the assortment on display were necklaces, earrings, belts, and bracelets. The real advantage, of course, lies in the fact that the jewelry will not tarnish.

The bright, permanent polish is obtained by dipping the jewelry in a tank containing an acid solution and passing an electric current through it. This electropolishing process, as it is called, leaves a brilliantly polished surface.—from the *Electromet Review*.

Darkroom Workbench

Designed especially to aid the industrial, medical, or scientific photographer, a new pamphlet entitled "Plans for Darkroom Workbench and Sink Units" is being offered free by the Eastman Kodak Company. The units described are designed to make cleaning as simple as possible and to eliminate dirt-catching constructional features. Planned to provide versatile accommodations for processing moderate amounts of photographic materials, the units may be built in any woodworking shop and moved to the location where they are to be used.

Pictorial Drafting

The principles of pictorial engineering drafting, as utilized in isometric and dimetric projection, are explained clearly and concisely in a 20-page illustrated booklet written by Paul F. Boehm and available without charge through the John R. Cassell Company, Inc., 110 West 42nd Street, New York 18, N. Y. In addition to illustrating and explaining the fundamentals of isometric and dimetric drawings, this new treatise also gives complete details of the new "Instrumaster" stencils which have been especially developed to make the construction of isometric and dimetric drawings not only faster and easier than possible with conventional methods but more accurate as well.

Photographic Murals

It is reported that photographic emulsions have been made which can be melted and painted on many types of surfaces, including walls. Photographic images can be made directly on such surfaces and developed.

Here and There in the Trade Literature[1]

THE June–July number of the *Dupont Magazine* contains three items of interest to us: an account of how "Chemistry brings television nearer," in which are described the contributions of chemistry to the development of the coaxial cables, the lenses, and the luminous phosphors; another on "Living with lucite," with gosamer illustrations; and finally an account of the 1946 program of Dupont fellowships, of which there are to be 41 in chemistry (including six post-doctoral ones) open this year to both men and women.

● The spring number of the *Educational Focus* discusses "Uses of optical equipment in the aluminum industry." After the following introduction, it goes on to describe in greater detail the uses and applications of the two instruments mentioned.

The rapid strides made by the aluminum industry in less than 60 years can be attributed in a large measure to various types of metallurgical equipment, among which are optical instruments for research and testing. Optical equipment literally serves as the "eyes" for the men who are working on metallurgical problems. Two of the outstanding optical instruments which have helped and will continue to help in making aluminum a better and more useful metal are the spectrograph and the metallograph.

● The new weed eradicator 2-4 D (2-4-dichlorophenoxyacetic acid) gets a good "going over" in the May *Dow Diamond*.

This weed-killing chemical with its tongue-twisting name does not kill in the ordinary sense by burning off top growth through toxic action. Chemists were aware of its peculiar properties before its weed control uses were discovered. It falls into the class of "synthetic hormones" or plant-growth regulators.

Early research work with this compound saw it applied to the leaves, flowers, and stems of many plants. When applied experimentally on the blossoms of fruit, it frequently increased the set and size of the fruit. Used on weeds, the chemical is not a rapid killer, but it kills with a high degree of certainty and thoroughness.

It appears to disturb the whole physiological balance of the plants. Immediately after application many plants grow with increased vigor, but the whole growth mechanism is thrown out of kilter; roots become enlarged and split, leaves take on fall colors, plants twist, curl, become distorted, and in a few weeks, dry up completely, die, and disintegrate—roots and all.

[1] For the company and address of a magazine cited, see THIS JOURNAL, January, 1946, p. 38.

● Here's one that is "off the record." If you tend to get seasick or airsick, you should read "Management of motion sickness" in the May *Therapeutic Notes*. At least you will know better what it is all about.

● We thought the following editorial from the June *Refinery News* worth reproducing:

DO WE LOVE WAR?

We fought a war. In fact we have won two wars, both being fought at the same time—one in Europe, one in the Pacific. During those hectic war years we prayed, worked, and sacrificed for peace. But now that we have had peace for approximately one year, do we really want it or do we love war?

That's a horrible realization for a people who confess loving peace, but witness the transformation that has occurred since the cessation of hostilities.

Our millions of servicemen who were engaged in the business of war and killing are now back home and at work. A year ago we searched every casualty list with a prayer, lest we see names of those we knew. We watched daily for the mailman to find out if our loved ones were still safe. We ought to thank God anew each day for His blessing of peace.

Yet, we read of nothing but dissension, bickering, griping in the world today. The casualty lists seem like a dream. The broken lives and hearts caused by those lists are coldly forgotten. We can't even think of those rows of white crosses as depicted on last month's *Refinery News* cover. What bothers us now is the lack of shirts, nylons, appliances, and new automobiles!

During the war production demands were almost fantastic. But we did it! We had to do it, or lose our Armies and Navies. We had to do it, so we put all our thought and energy and will power into doing it. We worked side by side, proud of our part, and worked together.

That's all over now and dead! Now it's "dog eat dog," every man for himself, selfishness, greed, mistrust—the human race seems cursed, strikes run rampant, discontent is prevalent, and how often the vet gets the short end of it!

We must love war for we gloried in it, we were human during it, we respected and helped others, we were true Americans. It's disgusting but unless we smarten up it'll be proved true.

As was recently said, "Unless we want peace as we wanted victory, more than anything else in life, enough to make any sacrifice for it, we may just as well begin now to prepare for the next war."

Or do we want and need that "next war" to live like a civilized people again? "War nostalgia," an article by J. G. Lucas, condensed in the April *Reader's Digest* from the *New York World Telegram*, presents that question from the G. I. point of view and states, "It is insane that war should bring out our best qualities and peace our worst." It *is* insane, but let's disprove that! Let's prove we love peace—rather than war!

• In an article entitled "The sciences: Tools in oil saving" in the *Lamp* for April one will find a lot of interesting applications of scientific methods in the field of petroleum technology. Elsewhere, a two-page colored map shows graphically "The world's oil," not only where it comes from but where it goes to. Another illustrated article, "Synthetic rubber workshop," shows some of the methods of processing, testing, and applying the new synthetic rubbers.

• It may be that some of our readers will be interested in the subject of the article, "Treating oil-water emulsions by heating," in the June *Rig & Reel.*

• It seems that one of the ways in which "margarine oils" differ from salad and cooking oils is that the natural amber color of the former has been removed by special bleaching processes. In fact, this is legally necessary in order that the vegetable oil shall not be subject (as colored margarine) to prohibitive taxes. This is certainly a strange state of affairs and called forth the following editorial comment in the May *Food Materials and Equipment.*

Here are lobbying and taxing power at their best. That government has the right to rule against artificial color in untaxed margarine we shall not question. The similarity of the colored product to dairy butter could easily work a deception on the consumer and a crippling injustice on the American dairy farmer. But to make it necessary that the natural pigmentation of American vegetable oils be removed is a bit thick. This natural pigmentation is closely allied to the carotene pigments which are the precursors of vitamin A. In removing it, the nutritive value of the oil is reduced. Subsequently, adding vitamin A in uncolored form does not meet the issue of the economic waste and injustice involved in destroying nutritive values in natural fats to appease the dairy bloc.

• From the June issue of the *Industrial Bulletin* of Arthur D. Little, Inc., comes the following:

SOWING WILD SPORES

Penicillin is now big business; 1945 production was valued at an estimated 100 million dollars, despite the drop in the wholesale price from 20 dollars to 60 cents for 100,000 units. Domestic needs are now being satisfied, and in March, 1946, 3 million dollars' worth of penicillin was shipped out of the country. .

Attainment of large-scale penicillin production during the war was a feat of industrial development appreciated only by those familiar with the early production in laboratory flasks and bottles. One turning point came when a strain of mold was found which would produce penicillin when agitated and aerated in large vats, rather than only when floating on the surface of the the nutrient medium, and another when a suitable medium was found for its growth. After submerged culture was proved practical, workers of the Department of Agriculture's Northern Regional Research Laboratory sought even better strains in the food markets and bakeries of Peoria, Illinois, and in the samples of moldy foods submitted by helpful housewives. They eventually found two—one on moldy cheese and the other on a cantaloupe. Thousands of other wild mold strains were investigated, but the strain now used for 99 per cent of the nation's penicillin production can be traced back to the one isolated from the Peoria cantaloupe. Two artificial mutations of this mold—one produced by X-ray and the other by ultraviolet light—have each doubled the yield of penicillin.

Generally molds are first grown on moist sterile bran, which is constantly aerated, so that each particle of bran offers its entire surface to support the growth. The mold spores are then used as "seed" to inoculate cultures in large tanks, nourished by a solution of corn steep liquor (a by-product of cornstarch production) and lactose (milk sugar). About 6 million pounds of lactose, valued at about $1,560,000, and 12 million pounds of corn steep liquor, valued at about $234,000, are used annually in the production of penicillin. The transfer of production from laboratory flasks to large-scale engineering processes and the development of more productive molds have resulted in the phenomenal increase in production and the drop in cost during the past few years.

Even now, the origin of penicillin is not entirely clear. It is known that there are least four kinds of penicillin, designated as F, G, K, and X, or, in Britain, I, II, III, and IV. The four types vary in therapeutic value, but the relative advantages of each have not been entirely established. Penicillin K has recently received adverse publicity, but until more evidence is available, there is no concerted effort being made toward production of one variety to the exclusion of others.

The production of sodium penicillin in crystalline form has recently been announced by Commercial Solvents Corporation. The product has high potency and is heat-stable, a real advantage, since penicillin as originally produced deteriorated rapidly enough to require dating and refrigeration. In fact, there has always been some concern over its shelf life. The new form will have an advantage only when packaged as dry penicillin since the improved stability is lost once the crystal form is destroyed. Specialties based on dissolved penicillin, for example, will not be improved by use of the new form.

Casual use of penicillin for minor ailments without medical supervision is considered questionable since small doses may kill only a portion of the germs present and leave alive those which are naturally most resistant to penicillin. The "penicillin-resistant" strain thus started may later prove dangerous. Apparently this phenomenon can be prevented to a large degree by the use of massive initial doses which establish high blood concentrations of penicillin with a resulting quick elimination of the disease organisms.

It has usually been necessary to hospitalize a patient for penicillin administration because frequent injections have been required, and oral administration is only 20 per cent as effective. Successful office treatments of single long-lasting daily injections which allow the patient to continue normal activities have been reported recently and should greatly widen the usefulness of penicillin for ambulatory subjects.

Despite the position of penicillin as the drug industry's leading product, other antibiotics are claiming a share of medical attention. Production of streptomycin is still so small that the drug must be carefully allocated to uses where most can be learned of its value. It is effective against many organisms which are not attacked by penicillin or the sulfa drugs. Although frequently reported as a cure for typhoid, it is at present considered to be limited in its effectiveness. Its principal value is in the treatment of tularemia, influenzal meningitis, and urinary tract infections. Remarkable recoveries from gastrointestinal surgery have been reported as a result of using a streptomycin-sulfa preparation, but this must be confirmed by further experience. A nutrient medium cheaper than the currently used beef extract is being sought for the organism which produces streptomycin. Another problem is the purification of streptomycin to eliminate histamine-like impurities which may produce undesirable effects when injected.

New types of antibiotics are constantly being discovered, but a complex procedure of clinical evaluation must be completed before they become available as therapeutics. Thus, subtilin and bacitracin, new bacterial products, are now undergoing wide experimentation. In the soil and the air and throughout the animal and vegetable world new antibiotics are being found which may be effective against specific organisms. For example, a wilt-resistant tomato was found to produce an antibiotic substance which inhibits certain fungi, while wild ginger, onions, burdock, and even buttercups have yielded interesting compounds. Active research by institutional, governmental, and commercial organizations is constantly broadening the field.

Report of the
NEW ENGLAND ASSOCIATION of CHEMISTRY TEACHERS

A Survey of Synthetic Medicinals

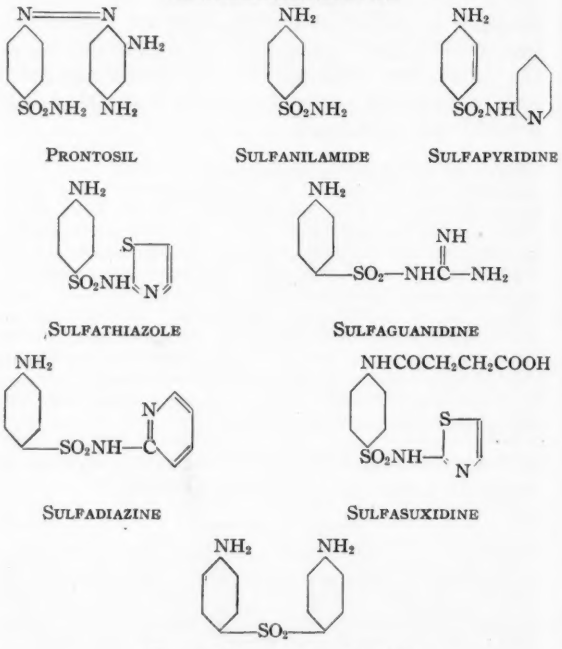
C. PAULINE BURT

Smith College, Northampton, Massachusetts

(*Continued from page 360*)

EACH way one turns in research on synthetic medicinals, one finds groups of chemists trying to change an existing molecule in order to produce better effects. Yet the first sulfa drug came, shall we say, out of the dye pot and not as a synthesis deliberately compounded to combat infections. We have heard much of sulfa drugs and seen them in use extensively; we can scarcely realize, therefore, that the first public report of the use of prontosil in Germany was as recent as 1933 and that its cleavage compound, sulfanilamide, was put on the market only in 1937. But sulfanilamide, prepared first in 1908, had been used in the dye industry almost 30 years before its efficacy as an antiseptic was demonstrated. One wonders how many effective substances the chemists right now have on the shelves. Perhaps we could inhibit cancer, cure tuberulosis, or completely banish malaria if we knew which bottle to reach for; perhaps we have not been as imaginative in this direction as we might have been. But once a molecule has been shown to demonstrate activity, the chemists have been very active. Since 1937 three or four thousand sulfa derivatives have been made and tested, and five or six are now in regular use. This achievement meant work at a feverish pitch in many laboratories; in the haste to produce good sulfa drugs, there was even much duplication of effort. For example, eight different companies applied for the patent on sulfathiazole when it first appeared.

SULFONAMIDE COMPOUNDS



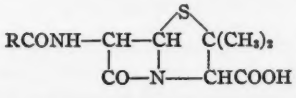
And yet from a standpoint of saving human lives, probably the amount of time spent in this research was not exorbitant. Sometime ago I tried to calculate the amount of time it would take to synthesize 3000 sulfa compounds, test them properly, and produce them so that they would be ready for a physician's use. I figured that, had one man been working alone (on a 12-hour day at that), it would have taken him 270 years to accomplish what was done with the sulfa drugs in six or seven years. Is it any wonder that such cocci as the pneumococcus, streptococcus, menigococcus, staphylococcus, and gonococcus, which had hitherto eluded all therapeutic measures, at last bowed their heads? This was indeed the first blitzkrieg of chemotherapy.

As yet penicillin is not a synthetic organic substance, but I do not doubt that it will be soon. Already the sulfa drugs have receded into the background, and newer substances are holding the foreground. Of the three antibiotics (penicillin, streptomycin, and streptothrycin) which have been studied sufficiently to warrant further research, penicillin was the first to be developed for actual use. It is the product of a humble mold, associated with types that we usually wish to get rid of rather than harbor. In 1929, well before the effects of prontosil were observed, Dr. Fleming of London noted the bacteriostatic effect of *Penicillin notatum* on *Staphylococcus aureus*. Attempts to grow and purify it for use gave such poor yields that the work was abandoned in 1932, not to be taken up again until 1939 and not to be raised to quantity production until 1944. Thus 15 years passed with this "miracle drug" waiting to be developed; once established, however, its value

was soon demonstrated. It is particularly effective against gram-positive cocci and bacilli but not against gram-negative. Streptococci, staphylococci, pneumococci, gonococci, meningococci, and spirochete infections are inhibited by it, but not the tubercle bacillus, malarial parasites, and many others. Research on its use in the treatment of syphilis is demonstrating that certain types of penicillin are effective Further findings, it is hoped, will prove that it is the "best and safest" treatment for the disease. Probably the most unique feature of penicillin is that its toxicity is practically negligible, and unfavorable reactions to it are rare. Since penicillin and the sulfa drugs are often indicated for the same purpose, the nontoxic penicillin is the favored one at present. It is usually administered intramuscularly, although local application has been tried with some success. As an unstable substance, it decomposes in the presence of gastric juice and on this account was for some time not used orally. However, methods of putting it up in tablet form so that it will pass through the stomach unaltered have been developed. The oral route cannot be used in all types of infections, and the dosage must be very large; nevertheless, it is a more convenient and less painful method of administration.

Although feverish research on methods of production had been under way since 1941, very little penicillin had been produced for use by January, 1943. The War Production Board had charge of allocation of the complete production from July, 1942, to August, 1945. During that time it was allocated both to research programs and to the Army, Navy, and Public Health Services. Production spiraled from practically zero early in 1943 to about 7000 billion units in December, 1945. This meant that enough had been produced and sufficiently purified to treat about seven million cases of pneumonia.

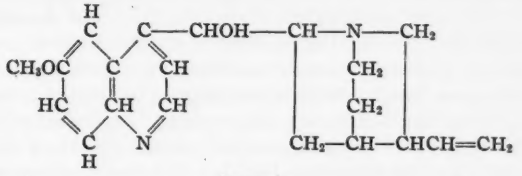
The coordinated research program on the chemistry and structure of penicillin has led to the isolation of five different but related types of penicillin. These types show specificities of action in different infections. For example, animal experimentation shows that type K is much less active in syphilis and in pneumonia than type G. Chemical structures of the penicillins have been suggested and published, though at this writing definite structures have not been agreed upon. The following is the structure published in December, 1945:



While some small amount of active material has been obtained, this structural compound has not yet been synthesized. Hence the production by fermentation still continues, and the large number of tremendous plants built for its production have not been scrapped.

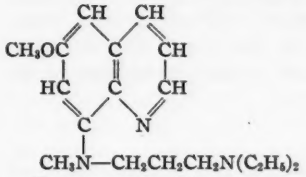
Nor do I think that we will just yet begin building plants to make synthetic quinine. For although quinine, the synthesis of which was reported in 1944, was as gravely needed for the armed forces as were penicillin and the sulfa drugs, the feasibility of putting together 48 atoms in the quinine pattern as a commercial venture was not then nor is it at present very great. But antimalarials we must have. Even before the war, it was estimated that there were in the world 800 million cases of malaria and three million deaths from it per year. In the United States alone, malaria was costing a half billion dollars annually. Even *with* quinine and atabrine available in sufficient quantities *before* the war, malaria was a problem, and when troops were moved into the malarial infested regions of the Pacific, it became a problem to the *n*th degree.

Since the mosquito transmits the disease to man, and man in turn transmits the disease to the mosquito, the most obvious ways of controlling the disease are to eliminate the mosquito and to control by treatment the

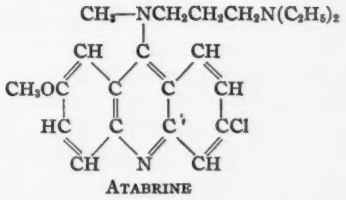


QUININE

infection in man. In the 19th century, swamps were drained "to improve the heathfulness" of communities, but this measure was not applied specifically to the control of malaria until the end of the century when it



PLASMOCHIN OR PAMAQUIN



ATABRINE

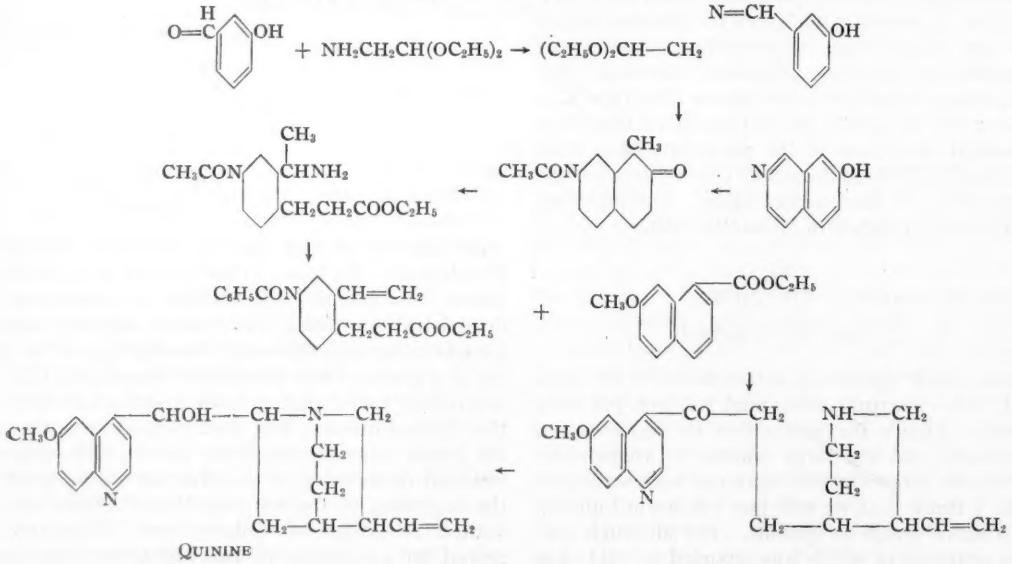
was definitely proved that the mosquito transmitted the parasite. In Cuba (1900) and in the Canal Zone (1910) the effectiveness of this measure was well demonstrated. Since then, many sanitary measures have been successfully used. Among these is the spraying of a powerful new insecticide known as DDT. But controlling the disease in man is also a necessity, and the alkaloid quinine, first used as a crude extract from the South American cinchona tree in 1630, very early assumed importance as an effective antimalarial. At the beginning of the war, the United States had only limited stockpiles of quinine but fortunately was geared for production of two synthetic antimalarials,

plasmochin and atabrine. Plasmochin, which is chemically related to quinine, was developed by the Germans and introduced as an antimalarial in 1926. It is much more effective than quinine, destroying the sexual forms of the parasites through which the mosquito spreads the disease. This represents an advantage over quinine and is important from the public health standpoint. Its margin of safety, however, is narrow, and it must be used under very strict supervision.

Atabrine, a yellow dye, was synthesized and developed by the Germans in 1930 and bears some similarity in structure to both plasmochin and quinine. Its activity is also more or less similar, but it does not completely destroy the sexual forms. It has an advantage over quinine in that it can be used prophylactically to prevent infection; its wide use for this purpose in the Pacific regions during the war is well known. Although neither quinine nor atabrine approach ideal antimalarials, it was nevertheless fortunate that our enemy, Germany, gave us the synthetic, atabrine, before our enemy, Japan, took away quinine. For although the chinchona tree, which is the source of quinine, was native to South America 300 years ago, exploitation by the local Latin despots gradually wiped out these forests. Had the far-seeing Dutch not started plantations in Java, the world would have been without quinine after the middle of the 19th century. And it was certainly by design that the Japanese took Java early in their campaign. They knew of malaria and its ravages in Burma, Malaya, the Philippines, and the islands of the South Pacific. They knew that the Allied armies could not fight in these places without antimalarials. It was therefore during the war years that atabrine assumed an important place as an antimalarial in its own right.

Also during the war years two chemists at Harvard University worked quietly in their laboratories and were able to announce in April, 1944, that they had put together from simple substances the very complicated quinine molecule which had resisted synthesis for 125 years. While this synthesis was an outstanding scientific achievement, the synthesis did not and does not yet mean that it is practical to produce quinine by this method. Yet in the course of these procedures reactions were studied and used, thus paving the way for simpler methods of synthesis not only of quinine but of other important organic substances. As in the case of penicillin, which was so vitally needed for the armed forces, a coordinated research program was set up in the United States (financed by the Office of Scientific Research and Development) with only one point in mind, the seeking of good antimalarials. The take-off point was the synthesis of compounds in the "image" of the active antimalarials, such as quinine, atabrine, and plasmochin. Parts of the work were allocated to dozens of different laboratories throughout the country, and a central place for screening these compounds was set up. Much of this program was kept completely secret until April, 1946, when the findings of this group of workers were presented to the Medicinal Section of the American Chemical Society for two and one-half days. Over 14,000 substances had been made and tested, including types that were not similar structurally to the known antimalarials. For example, new sulfa drugs, naphthaquinones, phenanthrenes, pyrimidines, and others were prepared and tested. Several compounds, which are definitely promising but have not yet been enough used clinically to be released to the general public, are known at present only by their test numbers, SN 13276 and SN 1796.

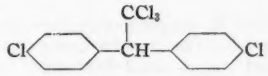
SOME OF THE INTERMEDIATE COMPOUNDS IN THE SYNTHESIS OF QUININE



QUININE

The need for antimalarials, though it has diminished with the end of the war, has not disappeared. There are many regions of the United States where malaria is rife. The Office of the Surgeon General of the United States Army, recognizing the fact that many of the returning veterans are infected, has issued an order that every veteran who has been in a malarious region should continue suppressive treatment with atabrine for at least four weeks after the last exposure, and that those who have had an attack of malaria should have suppressive medication for one to three months.

But to return to the subject of the parasites themselves. Obviously, it is better to attack the purveyor of the parasite than to wait for it to act and then try to cure the disease. Nor is malaria the only disease which is spread by insects, for typhus, cholera, yellow-fever, filariasis, bubonic plague, relapsing fever, dysenteries, and some other diseases as well, are spread by such insects as mosquitoes, fleas, flies, ticks, and other body lice. All these diseases have plagued man with gigantic death rates for centuries, and in time of war they are hazards as great as the enemy itself. Until 1942 safe and easy methods of destroying diabolical, disease-carrying pests were unknown. To be sure, the pyrethrum dusting powders were somewhat effective, but they had to be used in very high concentration, and even then they continued to be active only for a day or two. But in 1930 a Swiss chemist had dusted off a bottle which had been on the shelves since 1874 and proceeded to examine it as a mothproof agent, finally patenting it for this purpose in 1940, some 66 years after it was originally synthesized. Two years later some American entomologists discovered its remarkable qualities for killing a large variety of insects and pests. The substance is, of course, the now well-known DDT, an abbreviation for the lengthy chemical name, dichloro-diphenyl trichloroethane. This is the remarkable



DDT

chemical which, sprayed from low-flying planes, exterminated the insects on Saipan from one end of the island to the other, which was used in typhus-ridden Naples to delouse as many as 30,000 soldiers and civilians in one day, and which when merely sprinkled on clothing lasts until the next washing, or when impregnated in blankets persists through several washings, or when sprayed on an indoor wall continues to be efficacious for about three months. Its benefits to man in this war since 1942 are almost incalculable. The exact methods by which it acts, to be sure, are still unknown. It is a highly insoluble substance in water, and it is but little absorbed through the skin of the body. Although it appears to be somewhat toxic when taken internally, there is no great danger attendant upon its use as a delousing powder. Yet sprayed over large areas, it not only exterminates the harmful insects but also a great many useful insects upon which the agriculturist depends. Its usefulness to the farmer will presumably be determined by the success achieved in making its operation selective so that it can be directed against harmful insects alone. Still, it is possible that the problem of mosquito and fly control in community life is really solved, not only for great regions like New Jersey, but also for the small storekeeper and the householder, who will simply spray their walls with DDT every three months. And it is not inconceivable that, in time, DDT may reach all stagnant pools, swamps, and mosquito-infected islands so that the diseases of typhus and malaria, and consequently the need for atabrine and quinine, will be reduced to a negligible fraction.

I have tried to show you that with few exceptions *all* medicinals are now being made *synthetically* in the organic chemistry laboratory and that, for the most part, chemicals having the same general structure have like physiological effects. But I have had to leave out many alluring subjects, such as vitamins, hormones, antipyretics, analgesics, heart stimulants, and pressor substances. One thing is obvious, however, to any chemist and any layman. There is still much more work to be done in the medicinal field. For many diseases and malfunctions there is still no alleviation or cure; for many others, good medicinals do not yet exist. The problems which are still unsolved present a real challenge to chemists who have the will to work and an imaginative realization of the needs of the modern world.

TRAINING FOR TECHNICAL REPORT WRITING (*Continued from page 398*)

poraries have little or no opportunity to peep into his laboratory and criticize, but he then glibly exposes himself to every criticism by carelessly dashing off what first pops into his head. Is it not *his* creation—something to be proudly held aloft in knowledge of its superiority?

This whole deplorable situation can be improved by proper and adequate college training. It is true that if such training existed, the men who are already in industry would still be laboring under a disadvantage, but higher standards of writing would force better material from them, and the next generation would arrive at work better prepared to write. The entire trend of chemical writing can be changed from a collection of error-saturated material to writing that is at once clearly understandable and worthy of being taken at face value.

The author proposes that at least a one-hour course in technical report writing be required of all science and engineering students, even though it may have to replace part or all of a highly technical and specialized course in the plan of study.

RECENT BOOKS

THE CHEMICAL CONSTITUENTS OF PETROLEUM. *A. N. Sachanen*, Research and Development Division, Socony-Vacuum Oil Company, Inc. Reinhold Publishing Corporation, New York, 1946. 451 pp. 44 figs. 152 tables. 15.5 × 23.5 cm. $8.50.

The philosophy of the author in writing this book is well brought out by summarizing his preface. The ultimate goal of petroleum chemistry, he states, is to resolve petroleum into individual hydrocarbons and other constituents. For fractions above gasoline and perhaps light gas oils the problem of separating chemical individuals seems hopeless, so that the separation and quantitative determination of different classes of hydrocarbons and other constituents of petroleum is as important as the separation and identification of individual components.

The conventional classification of petroleum hydrocarbons into paraffins, naphthenes, aromatics, and unsaturates is followed as far as it is applicable; the author points out, however, that this classification, while quite sharp in the case of low and medium weight hydrocarbons, becomes ambiguous for those of high molecular weight. Such a substance, for example, as one containing both aromatic and naphthenic rings and long paraffinic side chains would possess predominant paraffinic, aromatic, or naphthenic properties, depending on the proportion of these structures in the molecule. This causes him to use methods of ring analysis for the characterization of high boiling fractions and products as well as for crude oils.

The author "does not pretend to be an impartial collector of data and views pertaining to the composition of petroleum." On problems which have not been crystallized into commonly accepted theories, he "has not hesitated to take a definite stand in the hope that such an attitude may be more useful in stimulating further efforts than an impartial accumulation of material." This attitude is one of the great merits of the book, which is not simply a collection of abstracts but a critical review, and is written with authority. While specialists may differ with some of the opinions expressed regarding their own fields, this does not detract from the essential accuracy of the book.

The successive chapters take up petroleum gases and natural gasoline, physical and chemical methods of determining hydrocarbons in distillates, hydrocarbons of straight-run and synthetic distillates, petroleum wax, oxygen, sulfur, and nitrogen compounds, resins and asphaltic compounds, classification of crude oils.

The abstracts are complete enough to allow a person not specializing in the exact field of work covered to get a good idea of what has been done. In a few cases, however, where detailed laboratory instructions are quoted this urge for completeness has been carried a little farther than seems desirable.

The book will be useful to workers in the petroleum industry, to persons studying to enter this industry, and to those who desire more than a casual acquaintance with petroleum as part of a general education.

In the section on synthetic rubber it is believed more attention should be paid to the work done by Americans in the development of synthetic rubber from butadiene, although detailed information in this field was probably not available on an unrestricted basis when the book was written.

The author hopes that this summary of information on the chemical constituents of petroleum will have a beneficial effect on future research, for as he thoughtfully points out, "New avenues of investigation are still open in the field of the chemical composition of petroleum. The investigation of coal tar developed the chemistry of aromatic hydrocarbons. It would be premature to predict the achievements which are deemed to be the issue of the investigation of petroleum, a much richer source of hydrocarbons and other constituents than coal tar, which is comparatively poor in the variety and number of its constituents. New methods and conspicuous improvements in classical methods open new possibilities in attacking problems related to the complex composition of petroleum. The enormous complexity of petroleum, though rather a drawback to investigation today, may become a great stimulus tomorrow."

C. D. LOWRY, JR.

UNIVERSAL OIL PRODUCTS COMPANY
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ELEMENTARY WAVE MECHANICS. *W. Heitler*, Professor of Theoretical Physics in the Dublin Institute for Advanced Studies. Oxford University Press, New York, 1945. viii + 136 pp. 37 figs. 10 tables. 12.5 × 18 cm. $2.25.

Students and teachers will welcome this brief but exact introduction to wave mechanics by one of the early masters and pioneers in wave-mechanical explanations of the chemical bond. The seemingly casual illustrations and the colorful grammatical expressions (*e. g.*, "sharp and unsharp" quantities) are the only deviations from a carefully written and logically organized presentation.

The book begins at the proper beginning for any exact science, with the experimental evidence, and concludes with two illuminating chapters on valency. Discrete quantum states and corresponding energy levels are demonstrated with the simple and clear case of a vibrating string.

In the "Problem of Two Electrons" Professor Heitler mathematically demonstrates the enduring identity of symmetric and antisymmetric combinations and their relation to the all-powerful Exclusion Principle. This leads into the exchange energy analysis which made the "Heitler-London-Slater-Pauling" combination world-famous. On the enigmatic question of just what "exchanges" or resonates or vibrates to cause a frequency shift and binding energy (since it cannot be the indistinguishable electrons in the pair), Heitler offers (p. 108) that it is "the frequency of exchange of spin directions." But since "spin" is just a consequence of relativity, this mysterious exchange phenomenon is still mysterious, "and it is better to accept it as a fundamental fact."

The book contains 37 simple illustrations, but the structure-curious chemist will feel the need for many more. Figure 22 is not a "charge cloud" but a radial distribution curve, which is a circular integration of the cloud. The important Figures 28 and 29, which explain the formation of a covalent bond, might have been much clearer if the "charge clouds" were represented by shading instead of by confusing circular lines, or better, by a series of shaded pictures showing the complete transition from separated atoms to the "united atom."

While the abstract mathematical retreats have been kept to a minimum, it is this reviewer's student-minded opinion that certain explanations might have been still more emphatic with such pictorial realism as that mentioned above. For example, it is not really obvious that "we can multiply every wave function by an arbitrary factor without changing its physical meaning" (p. 66), but it should be strikingly obvious that we can magnify the equivalent wave *pattern* to any extent without changing its "eigenshape" or characteristic shape.

The complete absence of misprints and errors, in spite of the occasional mathematical "red tape," is a tribute to both the author and printers of this wartime publication. The book should be added to every library of physical and theoretical chemistry.

WILLIAM J. WISWESSER

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